Intermolecular Pair Potentials
in the Theoretical Description of Fluids
and Fluid Mixtures

By

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Abstract of Dissertation Presented to the
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INTERMOLECULAR PAIR POTENTIALS
IN THE THEORETICAL DESCRIPTION OF FLUIDS
AND FLUID MIXTURES

By

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        In order to use modern molecular theories of fluids or solids

one requires information about the intermolecular pair potential. The

goal of the present work has been to provide such information for use

in the prediction of properties of fluids and fluid mixtures. General

features of empirical algebraic expressions for the intermolecular

pair potential in fluids have been investigated. Both the like-pair

potential energy (mutual energy of a pair of molecules of the same

species) and the unlike-pair potential energy (mutual energy of a pair

of molecules of different species) have been studied. The pairwise

additivity approximation for configurational energy is assumed through-

out this work.

        Formulae for the unlike-pair parameters in terms of the like-

pair parameters for the Mie (n,6) potential energy model are examined

for their abilities to predict cross-term second virial coefficients.

The London dispersion formula and an assumption of geometric mean

repulsion energies are shown to apply only for cases wherein the

repulsion exponent n is not very different for the pairs of molecules. A geometric mean rule for each one of the three parameters is shown to have far more general applicability and high accuracy in predicting the cross-term second virial coefficient. The geometric mean rule for the energy and distance parameters is also shown to perform well for predicting the cross-term second virial coefficient for molecules described by the Dymond and Alder potential energy function.

The set of geometric mean rules for all Mie (n,6) parameters is called the total geometric mean rule. These rules may also be adapted to predict cross-term second virial coefficients for the exponential-6 potential. Relationships developed between parameters for the Mie (n,6) potential and the exponential-6 potential show that the three parameters in the latter $(\varepsilon, r_m, \alpha)$ can reasonably be equated to three parameters (ε, r_m, n) in the (n,6) potential. Furthermore, the implied equivalence of these potential parameters suggests that the unlike-pair parameters for the exponential-6 potential should follow the total geometric mean rule. This set of rules predicts good values for the cross-term second virial coefficients in six systems tested.

The perturbation theory of Barker and Henderson has been used to test various Mie (n,6) intermolecular pair potentials for their ability to predict liquid properties. It is shown that it is possible to obtain a considerable improvement in predicted liquid properties when n is allowed to vary from the value 12 usually assigned to this parameter.

Two new prescriptions are developed for calculating mixture potential energy parameters for use with the one-fluid or two-fluid

theories of mixtures. The van der Waals prescription is shown to be a special case of one of these new prescriptions. It is further shown that the total geometric mean rule found to work for the Mie (n,6) potential in the gas phase can be used indirectly to predict the excess properties of liquid mixtures in the one-fluid theory. The method used obviates the empirical determination of the unlike-pair potential energy parameters. A method is developed for obtaining both like-pair and unlike-pair potential parameters which are independent of the choice of reference fluids. The necessity is demonstrated for accounting for the particular (n,6) potentials required for each molecule in liquid mixture calculations, and two successful methods are proposed for doing so.

CHAPTER 1

INTRODUCTION

Statistical mechanical theories of fluids relate experimentally observed thermodynamic properties to the potential energy between pairs of molecules. These theories have reached a level of development such that further refinements in their ability of these theories to predict thermodynamic properties of fluids and fluid mixtures may result mainly from the use of improved models for the intermolecular pair potentials.

The present work is intended to demonstrate the benefits derived from using a different pair potential characteristic of each molecular species in accurate theories of fluids and fluid mixtures. General features of empirical algebraic expressions for the inter-molecular pair potential have been investigated. The first part of this work (Chapters 2, 3 and 4) is concerned with models for accurate intermolecular pair potentials in pure and mixed gases. The models studied most extensively are the Mie (n,6) potentials. Those dealt with less extensively are the exponential-6 potential and the Dymond-Alder potential. Like-pair potential parameters for various molecules are obtained from second virial coefficients of pure gases. For the potential models studied methods have been developed for estimating the unlike-pair potential parameters which characterize the interaction between a pair of molecules of different species from the like-pair parameters of the respective molecules. The resulting unlike-pair potential parameters are used to calculate accurate values of cross-term second virial coefficients in gas mixtures.

In the remaining chapters information gained in Chapters 2, 3 and 4 is used in the determination of effective pair potentials for use in pairwise additive theories of pure and mixed liquids. Only (n,6) potentials are used for the liquid studies. Effective pair potentials have been found (Chapter 5) which when used in a perturbation theory of the liquid give good estimates for the residual internal energy and entropy of several liquids. In this part of the liquid study parameters for the various (n,6) potentials are those determined from the second virial coefficients of the respective species. In general for a particular molecular species the (n,6) potential found to give the best estimates of liquid properties is not the same (n,6) potential found to give the best estimates of second virial coefficients.

It is demonstrated (Chapter 6) that the methods found to give good estimates of the unlike-pair parameters in the gas phase can be used indirectly to estimate unlike-pair parameters for use with the liquid phase potentials. The importance in liquid mixture calculations of accounting for the interaction of molecules with different pair potentials is emphasized with reference to the particular case of the methane + perfluoromethane system. A simple method is proposed for accurately estimating the excess properties of such mixtures.

It is further shown (Chapter 7) that statistical mechanics provides relationships for calculating composition-dependent potential parameters for use in the one-fluid and two-fluid theories of liquid mixtures. The new prescriptions called the virial coefficient prescriptions are shown to give accurate estimates of the properties of

mixtures of (12,6) molecules in both the gas phase and the liquid phase. One of the new prescriptions, the virial coefficient Boyle (vcB) prescription, is shown to be for real systems the analog of the van der Waals prescription for van der Waals systems. Methods are developed for using the vcB prescription to predict either accurate estimates of the excess properties or accurate estimates of both mixture properties and excess properties when the component molecules obey different (n,6) potentials.

In Chapter 8 methods developed in previous chapters are combined to demonstrate that it is possible with knowledge of only the gas phase (n,6) potentials of pure components to make accurate estimates of the excess properties of liquid mixtures. The mixtures studied exhibit behavior ranging from nearly ideal to very nonideal. The results provide an explanation for the deviation of the unlike-pair energy parameter ϵ_{ij} from the geometric mean of the respective like-pair parameters which is observed in mixture calculations where all molecules are assumed to obey the same pair potential.

CHAPTER 2

MIXTURE RULES FOR THE MIE (n,6) INTERMOLECULAR PAIR
POTENTIAL AND THE DYMOND-ALDER PAIR POTENTIAL

Introduction

The Mie (n,6) model for the intermolecular pair potential
function is of the form

$$\cdot \phi(r) = \frac{B}{r^n} - \frac{A}{r^6} \tag{1}$$

It has been studied in some detail for argon and nitrogen by Klein and
Hanley[1,2] and for methane by Ahlert, Biguria and Gaston.[3] The repulsion-
term exponent n as a third adjustable parameter gives this model a
flexibility equivalent to that of other three-parameter models,[2] in a
simple analytical form. The coefficients A and B in Eq. (1) may be
written in terms of the parameters ϵ and σ, the depth of the potential
minimum and the intermolecular separation at which $\phi(r) = 0$, respectively,

$$A = \left(\frac{n^n}{6^6} \right)^{\frac{1}{n-6}} \left(\frac{\epsilon \sigma^6}{n-6} \right) \tag{2}$$

and

$$B = \left(\frac{n^n}{6^6} \right)^{\frac{1}{n-6}} \left(\frac{\epsilon \sigma^n}{n-6} \right) \cdot \tag{3}$$

Alternatively the coefficients may be expressed in terms of ϵ and r_m,
where r_m is the intermolecular separation at which $\phi(r) = -\epsilon$,

$$A = \frac{n \epsilon \, r_m^6}{n-6} \tag{4}$$

and

4

$$B = \frac{6\epsilon \, r_m^n}{n-6} \, .$$ (5)

The most familiar form of the Mie (n,6) potential is the Lennard-Jones potential in which n is 12.

Unlike-Pair Potential

From the leading term in the London theory of dispersion forces[4] the unlike-pair attraction coefficient A_{ij} (Note that the double subscript "ij" will refer to the unlike-pair intermolecular interaction and the single subscript "i" or "j" will refer to the like-pair intermolecular interaction.) may be written as

$$A_{ij} = (A_i A_j)^{1/2} f_I \, ,$$ (6)

where

$$f_I = \frac{2(I_i I_j)^{1/2}}{(I_i + I_j)} .$$ (7)

and I is the ionization potential.

The theory for the repulsion interaction is not well developed; however, one combining rule has been proposed by Amdur, Mason and Harkness[5] based on molecular beam scattering results. Mason and co-workers use a purely repulsive potential of the form

$$\phi_i = B_i r^{-n_i}$$ (8)

to represent the intermolecular interaction at small separations. For the unlike-pair repulsion interaction they suggest that

$$\phi_{ij}^{rep} = (\phi_i^{rep} \phi_j^{rep})^{1/2}$$ (9)

or

$$\frac{B_{ij}}{r^{n_{ij}}} = \left(\frac{B_i B_j}{r^{n_i} . r^{n_j}} \right)^{1/2} . \tag{10}$$

With this assumption dimensional considerations require that

$$n_{ij} = (n_i + n_j)/2 \tag{11}$$

and therefore,

$$B_{ij} = (B_i B_j)^{1/2} . \tag{12}$$

Abrahamson[6] has made theoretical calculations of the interatomic repulsion interaction of both like and unlike inert gas atoms. These calculations were based on the Thomas-Fermi-Dirac statistical model of the atom and show Eq. (9) to be satisfied to within a few percent.

Semitheoretical Mixture Rules

Using Eq. (6) for the unlike attraction energy and Eq. (9) for the unlike repulsion energy, the appropriate mixture rules for the parameters ε, n, and r_m (or σ) may be derived for the Mie (n,6) potential.

Using Eqs. (12), (11) and (5)

$$B_{ij} = \frac{6\varepsilon_{ij} \, r_{m_{ij}}^{n_{ij}}}{n_{ij} - 6} = \left[\left(\frac{6\varepsilon_i \, r_{m_i}^{n_i}}{n_i - 6} \right) \left(\frac{6\varepsilon_j \, r_{m_j}^{n_j}}{n_j - 6} \right) \right]^{1/2} \tag{13}$$

or

$$\varepsilon_{ij} = (\varepsilon_i \varepsilon_j)^{1/2} \frac{\left(r_{m_i}^{n_i} r_{m_j}^{n_j} \right)^{1/2}}{r_{m_{ij}}^{n_{ij}}} \frac{(n_{ij} - 6)}{[(n_i-6)(n_j-6)]^{1/2}} . \tag{14}$$

Similarly with Eq. (6) and Eq. (4)

$$A_{ij} = \frac{n_{ij}\varepsilon_{ij}r_{m_{ij}}^6}{n_{ij} - 6} = \left[\left(\frac{\varepsilon_i n_i r_{m_i}^6}{n_i - 6}\right)\left(\frac{\varepsilon_j n_j r_{m_j}^6}{n_j - 6}\right)\right]^{1/2} f_I \tag{15}$$

or

$$\varepsilon_{ij} = (\varepsilon_i \varepsilon_j)^{1/2} f_n f_I \frac{(n_{ij} - 6)}{[(n_i-6)(n_j-6)]^{1/2}}\left[\frac{\left(r_{m_i} r_{m_j}\right)^{1/2}}{r_{m_{ij}}}\right]^6 \tag{16}$$

where

$$f_n = \frac{(n_i n_j)^{1/2}}{n_{ij}} = \frac{2(n_i n_j)^{1/2}}{(n_i + n_j)} \quad . \tag{17}$$

Elimination of ε_{ij} between Eqs. (14) and (16) yields after algebraic manipulation

$$r_{m_{ij}} = \left(r_{m_i}^{n_i-6} \, r_{m_j}^{n_j-6}\right)^{\frac{1}{2(n_{ij}-6)}} (f_n f_I)^{\frac{1}{6-n_{ij}}} \quad . \tag{18}$$

Note that for the very special case where $f_n = 1$ ($n_i = n_j$) and $f_I = 1$ we have from Eq. (18)

$$r_{m_{ij}} = (r_{m_i} r_{m_j})^{1/2} \quad \text{and} \quad \sigma_{ij} = (\sigma_i \sigma_j)^{1/2} \quad , \tag{19}$$

and from Eq. (16)

$$\varepsilon_{ij} = (\varepsilon_i \varepsilon_j)^{1/2} \quad . \tag{20}$$

These rules, Eqs. (19) and (20), are those proposed by Lehman[7] and later by Good and Hope.[8] It should be mentioned that due to the relationship between σ and r_m these two quantities will obey the same mixture rule only when $n_i = n_j$.

The performance of the semitheoretical mixture rules for ε_{ij},

n_{ij} and $r_{m_{ij}}$ given in Eqs. (11), (16), (18) has been tested in seven

binary gas mixtures. Pure component parameters (Table 1) were

determined from a fit of the second virial coefficient (see Appendix A).

The cross-term second virial coefficient was calculated using the semi-

theoretical values of ε_{ij}, n_{ij} and σ_{ij} (Table 2) and compared with

experiment. The results can be interpreted as a test of the assumptions

given in Eqs. (6) and (9) within the framework of the Mie (n,6)

potential. These results, shown in Table 3, are poor in all but two

cases, the Ar + CH_4 and Ar + N_2 mixtures. Both of these may be regarded

as special cases in which f_n and f_I are nearly equal to 1.

Empirical Mixture Rules

As an alternative to the unsuccessful rules proposed above

purely empirical mixture rules were found which could be applied in

all cases including those in which n_i and n_j differ greatly. The

limited success of the semitheoretical rules suggests that in case

$n_i = n_j$ and $I_i = I_j$ the unlike-pair energy and distance parameters

should be the simple geometric mean of the respective like-pair

parameters. Such simplicity while appealing is hardly a basis for

choosing these forms. However, results of a least squares fit of

the cross-term second virial coefficient for the CH_4 + CF_4 system

shown in Table 2 indicate that the best-fit results are reasonably

reproduced by the geometric mean ε and σ. If then the geometric mean

is retained for these two parameters, the choice of a proper mixture

rule for the n's is all that remains.

The semitheoretical rules lead to the unlike repulsion exponent

Table 1. Pure component parameters.

Component	ϵ/k(°K)	σ(Å)	n	I(eV)	Temperature range (°K)	rms dev(cm³/mole)	Ref.
Argon[a]	169.8	3.225	20.00	15.68	87.12 - 873.15	0.48	b,c,d,e
Nitrogen	133.35	3.532	19.31	15.51	75.0 - 700.0	0.79	f
Methane[g]	218.0	3.568	21.0	13.16	120.0 - 600.0	not reported	h
Methane[i]	236.39	3.533	25.03	13.16	273.16 - 623.16	0.04	j
Ethane	273.82	4.606	17.74	11.65	220.0 - 500.0	1.30	f
Neopentane	651.92	5.760	111.89	10.55	303.16 - 548.16	1.41	k,l,m
Perfluoromethane	373.31	4.186	136.30	17.81	273.16 - 623.16	0.12	j
Sulfur hexafluoride	485.30	4.969	138.68	19.3	280.0 - 520.0	1.07	f

[a]This set of parameters obtained by D. Vives and J. P. O'Connell at the University of Florida from a least squares fit.

[b]R. D. Weir, I. W. Jones, J. S. Rowlinson, and G. Saville, Trans. Faraday Soc. 63, 1320 (1967).

[c]E. Whalley, Y. Lupien, and W. G. Schneider, Can. J. Chem. 31, 722 (1953).

[d]A. Michels, Hub. Wijker, and H. K. Wijker, Physica 15, 627 (1949).

[e]A. Michels, J. M. Levelt, and W. DeGraaff, Physica 24, 659 (1958).

[f]J. H. Dymond and E. B. Smith, The Virial Coefficients of Gases (Clarendon, Oxford, 1969).

[g]This set of parameters was given by Ahlert, Gaston, and Biguria, Ref. 3. These parameters were used for all mixture calculations except those with the CH_4 + CF_4 mixture.

[h]See Ref. 3.

[i]This set of parameters determined by least squares fit of the data in Footnote j. These parameters were used for the CH_4 + CF_4 mixture calculations only.

[j]D. R. Douslin, R. H. Harrison, and R. T. Moore, J. Phys. Chem. 71, 3477 (1967).

Table 1 (Continued)

[k] J. A. Beattie, D. R. Douslin, and S. W. Levine, J. Chem. Phys. 20, 1619 (1952).

[l] S. D. Hamann and J. A. Lambert, Australian J. Chem. 7, 1 (1954).

[m] S. D. Hamann, J. A. Lambert, and R. B. Thomas, Australian J. Chem. 8, 149 (1955).

Table 2. Unlike potential parameters.

System		ε_{ij}/k (°K)	σ_{ij} (Å)	n_{ij}
$CH_4 + Ar$	semitheo	189.41	3.399	20.50
	set A	192.40	3.392	20.49
	set B	192.40	3.392	20.50
$CH_4 + C_2H_6$	semitheo	268.95	3.992	19.37
	set A	244.32	4.054	19.30
	set B	244.32	4.054	19.37
$CH_4 + C(CH_3)_4$	semitheo	154.90	5.427	66.45
	set A	376.99	4.533	48.47
	set B	376.99	4.533	66.45
$CH_4 + CF_4$[a]	best fit	289.74	3.847	59.54
	semitheo	238.28	4.097	80.67
	set A	297.06	3.846	58.41
	set B	297.06	3.846	80.67
$CH_4 + SF_6$	semitheo	180.73	4.806	79.84
	set A	325.26	4.211	53.97
	set B	325.26	4.211	79.84
$N_2 + Ar$	semitheo	151.88	3.370	19.66
	set A	150.48	3.375	19.65
	set B	150.48	3.375	19.66
$N_2 + C_2H_6$	semitheo	198.82	4.001	18.53
	set A	191.09	4.033	18.51
	set B	191.09	4.033	18.53

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[a]Determined by least squares fit of cross-term second virial coefficient. Root mean square deviation = 0.09 cm^3/mole.

Table 3. Cross virial coefficient B_{12} with the (n,6) Mie potential.

Mixture components	Temp. (°K)	Exptl.	Semi-theoretical Eqs. (11), (16), (18)	Empirical rules Set A	Set B	Ref.
CH_4+Ar[a]	142.60	-138.6	-135.1	-138.3	-138.3	b
	176.70	- 86.7	- 89.2	- 91.5	- 91.5	
f_I = .9962	239.80	- 48.1	- 46.3	- 47.8	- 47.7	
	295.00	- 26.9	- 26.5	- 27.6	- 27.6	
	rms dev		2.4	2.4	2.4	
$CH_4+C_2H_6$	273.20	-111.9	-127.6	-110.0	-109.6	c
	298.20	- 92.0	-106.6	- 90.9	- 90.5	
f_I = .9981	323.20	- 75.6	- 89.5	- 75.4	- 75.1	
	rms dev		14.75	1.27	1.61	
$CH_4+C(CH_3)_4$	303.2	-165.0	42.2	-167.7	-144.3	c
	323.2	-138.0	52.4	-144.7	-123.4	
f_I = .9939	333.2	-132.0	57.0	-134.6	-114.1	
	343.2	-118.0	61.3	-125.2	-105.5	
	353.2	-113.0	65.3	-116.6	- 97.6	
	363.2	-106.0	69.0	-108.5	- 90.2	
	383.2	- 93.0	75.9	- 94.0	- 76.9	
	403.2	- 78.0	82.0	- 81.3	- 65.3	
	rms dev		181.5	4.2	15.9	
CH_4+CF_4	273.16	- 62.07	- 32.13	- 67.19	- 56.95	d
	298.16	- 48.48	- 20.54	- 52.81	- 43.67	
f_I = .9887	323.16	- 37.36	- 11.08	- 41.19	- 32.92	
	348.16	- 28.31	- 3.20	- 31.60	- 24.04	
	373.16	- 20.43	3.45	- 23.57	- 16.59	
	398.16	- 13.98	9.15	- 16.74	- 10.25	
	423.16	- 8.33	14.08	- 10.87	- 4.79	
	448.16	- 3.21	18.38	- 5.76	- .04	
	473.16	1.02	22.17	- 1.28	4.13	
	498.16	4.94	25.53	2.68	7.82	
	523.16	8.28	28.54	6.21	11.10	
	548.16	11.39	31.24	9.37	14.05	
	573.16	14.10	33.67	12.21	16.71	
	598.16	16.55	35.88	14.79	19.11	
	623.16	18.88	37.90	17.13	21.30	
	rms dev		22.90	2.94	3.56	

Table 3 (Continued)

Mixture components	Temp. (°K)	Exptl.	B_{12} (cm^3/mole)			Ref.
			Semi-theoretical Eqs. (11), (16), (18).	Empirical rules Set A	Set B	
CH_4+SF_6	313.2	– 85.0	19.3	– 81.6	– 65.6	e
	333.2	– 68.0	27.1	– 68.7	– 53.9	
f_I = .9819	353.2	– 57.0	33.8	– 57.6	– 43.8	
	373.2	– 45.0	39.7	– 47.9	– 35.0	
	393.2	– 33.0	45.0	– 39.4	– 27.3	
	rms dev		91.0	3.5	13.3	
N_2+Ar	148.2	– 81.6	– 82.2	– 81.1	– 81.1	f
	173.2	– 59.1	– 59.6	– 58.7	– 58.6	
f_I = 1.00	198.2	– 44.0	– 43.9	– 43.1	– 43.1	
	223.2	– 32.6	– 32.4	– 31.7	– 31.7	
	248.2	– 23.7	– 23.6	– 23.0	– 23.0	
	273.2	– 16.4	– 16.7	– 16.2	– 16.2	
	298.2	– 10.9	– 11.2	– 10.7	– 10.6	
	323.2	– 6.2	– 6.6	– 6.1	– 6.1	
	rms dev		0.4	0.6	0.6	
$N_2+C_2H_6$	277.6	– 65.4	– 66.3	– 61.7	– 61.6	c
	310.9	– 38.6	– 49.1	– 45.0	– 44.9	
f_I = .9898	377.6	– 20.1	– 25.2	– 21.0	– 21.6	
	444.3	– 3.8	– 9.4	– 6.4	– 6.3	
	510.9	5.9	1.7	4.4	4.5	
	rms dev		6.1	3.6	3.6	

[a]The lowest temperature point has not been included as there appear to be errors in the calculation of the reported B_{12} for this point in Footnote b.

[b]G. Thomaes, R. van Steen Winkel, and W. Stone, Mol. Phys. 5, 301 (1962).

[c]R. D. Gunn, M.S. thesis, University of California, Berkeley, 1958.

[d]See Footnote j, Table 1.

[e]S. D. Hamann, J. A. Lambert, and P. B. Thomas, Australian J. Chem. 8, 149 (1955).

[f]J. Brewer and G. W. Vaughn, J. Chem. Phys. 50, 2960 (1969).

being the arithmetic mean of the two like repulsion exponents (Eq. 11).
Once again, however, a glance at the least square mixture parameters
for $CH_4 + CF_4$ reveals that the value of 59.54 for the unlike repulsion
exponent is very nearly the value 58.41 obtained as the geometric mean
of the two like repulsion exponents. As a result two sets of empirical
rules were examined.

Set A	Set B
$\epsilon_{ij} = (\epsilon_i \epsilon_j)^{1/2}$	$\epsilon_{ij} = (\epsilon_i \epsilon_j)^{1/2}$
$\sigma_{ij} = (\sigma_i \sigma_j)^{1/2}$	$\sigma_{ij} = (\sigma_i \sigma_j)^{1/2}$
$n_{ij} = (n_i n_j)^{1/2}$	$n_{ij} = (n_i + n_j)/2$

The results of calculating B_{12}, the cross-term second virial coeffi-
cient, for the two sets of empirical rules are reported in Table 3.
The superiority of the total geometric mean rule, set A, is apparent.
This set of rules appears to be generally applicable to all of the
mixtures tested. The root-mean-square deviations of 0.6 to 4.2 cm^3/mole
appear to be within the accuracy to which the experimental values are
known. This is quite significant in the light of the great differences
in molecular character represented by some of the mixtures.

Other sets of rules have been tested, though not reported here.
One such set of rules is one in which each of the unlike parameters is
the arithmetic mean of the respective pure component parameters. This
set of rules performed remarkably well for the $CH_4 + CF_4$ system with
a root-mean-square deviation of only 1.06 cm^3/mole. However, this

particular set of rules failed to exhibit the general applicability found for the rules given in set A.

The Dymond-Alder Potential

For molecules which obey the same form of the reduced pair potential energy function $\phi^*(r^*)$, where $\phi^* = \phi/\epsilon$ and $r^* = r/r_m$, the empirical rules always require the unlike-pair energy and distance parameters ϵ and r_m (or σ) to be the simple geometric mean. For the Mie (n,6) potential this is the case where $n_i = n_j$. This result, however, is not restricted to the Mie (n,6) potential. The Dymond and Alder numerical potential energy function[9] for argon has been shown by Reed and Gubbins[10] to perform well for the other inert gases and for O_2, N_2 and CH_4 but not for CF_4. The potential energy parameters (ϵ, σ) for the other molecules are obtained from the argon parameters by corresponding states relationships. Results of predicting the cross-term second virial coefficient for four binary gas mixtures using the geometric mean rule for ϵ and σ and the tabulated reduced second virial coefficients for the Dymond and Alder potential are presented in Table 4. The results are excellent.

Conclusions

Within the framework of the Mie (n,6) potential the assumption of a geometric mean unlike repulsion energy, Eq. (9), and a corrected geometric mean attraction energy, Eq. (6), predicts the correct cross-term second virial coefficient only for those cases where these rules are equivalent to the geometric mean rule for all parameters. The

Table 4. Cross virial coefficient B_{12} with the Dymond and Alder potential.[12]

B_{12} (cm^3/mole)

Mixture components	Temp. (°K)	Exptl.	Geometric mean rule	Ref.
CH$_4$ + Ar	142.6	-138.6	-138.1	a
	176.7	- 86.7	- 91.2	
	239.8	- 48.1	- 47.4	
	295.0	- 26.9	- 27.3	
	rms dev		2.3	
N$_2$ + Ar	90.0[b]	-213.9	-212.72	c, d
	148.16	- 81.58	- 82.07	
	173.16	- 59.13	- 59.32	
	198.16	- 43.96	- 43.61	
	223.16	- 32.56	- 32.13	
	248.16	- 23.73	- 23.41	
	273.16	- 16.43	- 16.57	
	298.16	- 10.88	- 11.08	
	323.16	- 6.19	- 6.51	
	rms dev		0.50	
Ar + O$_2$	90.0[b]	-233.3	-235.3	d
N$_2$ + O$_2$	90.0[b]	-222.2	-216.9	d

[a]See Footnote b, Table 3.

[b]These experimental values of B_{12} were calculated from the excess second virial coefficient $E = B_{12} - \frac{1}{2}(B_{11} + B_{22})$ reported in Footnote d with B_{11} and B_{22} calculated from the Dymond and Alder Potential. The authors Knobler et al. of Footnote d originally calculated B_{11} and B_{22} using the Lennard-Jones (12,6) potential.

[c]See Footnote f, Table 3.

[d]C. M. Knobler, J. J. M. Beenakker, and H. F. P. Knaap, Physica 25, 909 (1959).

set A of rules, in which each parameter (ε, σ, n) is the geometric mean of the respective pure component parameter, works well for all of the binary gas mixtures studied. The significance of the results may be seen in that sets of the three Mie parameters for like-pair inter-molecular interaction allow the prediction of binary mixture properties without any knowledge of mixture properties. This is in contrast to the use of a two-parameter potential for the like-pair interaction which has been shown by Eckert, Renon, and Prausnitz[11] to require the use of a third parameter (equivalent to f_I) obtained from binary mixture data to correlate mixture data.

The empirical rules in set A or set B suggest that when molecules obey the same form of the pair potential the mixing rules for the energy and distance parameters should be the geometric mean. This is supported by the agreement between calculated and experimental cross-term second virial coefficients of mixtures of molecules which obey the Dymond and Alder numerical potential.

Sherwood and Prausnitz[12] computed values of the third virial coefficient for two special cases of the Mie (n,6) potential with parameters (ε, σ) determined from least squares fits of the second virial coefficient. These are the Lennard-Jones (12,6) potential and the Sutherland (∞,6) potential. Where the third virial coefficient of a pure system has been calculated with both the Lennard-Jones and Sutherland potentials, the values predicted by the (12,6) potential are higher than experimental data, while the values predicted by the (∞,6) potential are lower than experimental data. The (n,6) potentials

reported in the present chapter for pure systems have values of n
ranging from 17.74 for ethane to 138.68 for sulfur hexafluoride. These
potentials will predict values for the third virial coefficient which
fall in the range where the experimental values lie, between those
predicted by the Lennard-Jones and Sutherland potentials.

CHAPTER 3

A MIXTURE RULE FOR THE EXPONENTIAL-6 POTENTIAL

Introduction

It was shown in the previous chapter that for the Mie $(n,6)$ intermolecular pair potential the unlike-pair parameters $(\varepsilon_{ij}, \sigma_{ij}, n_{ij})$ are the geometric mean of the respective like-pair parameters for second virial coefficients. It is shown below that these mixture rules can be extended to define mixture rules for the exponential-6 potential,

$$\phi(r) = \frac{\varepsilon}{(1-6/\alpha)} \left[\frac{6}{\alpha} \exp[\alpha(1 - r/r_m)] - (r_m/r)^6 \right] . \quad (21)$$

Here r_m is the value of r at which $\phi(r) = -\varepsilon$. The value of r at which $\phi(r) = 0$ (i.e., $r = \sigma$) can be determined from r_m by solving the following equation numerically.[13]

$$\ln(\sigma/r_m) = -(1/6)\{\ln(6/\alpha) + \alpha(1-\sigma/r_m)\} . \quad (22)$$

Mixture Rules

Since ε and σ in the exponential-6 potential have the same meaning in the Mie $(n,6)$ potential it is reasonable to assume that these parameters will obey the same mixture rule for both potentials. An estimate of the third parameter α for the unlike pair may be obtained in the following way.

In the $(n,6)$ potential the repulsive energy is of the form

$$\phi(r)^{\underline{rep}} = Br^{-n} \quad (23)$$

where B is constant. From (23) we have

$$\frac{d \ln \phi^{\overline{rep}}}{d \ln r} = -n \quad .$$
(24)

For the exponential-6 potential the form is

$$\phi(r)^{\overline{rep}} = Ke^{-br}$$
(25)

and

$$\frac{d \ln \phi^{\overline{rep}}}{d \ln r} = -br \quad .$$
(26)

The results of the (n,6) mixture rule study (geometric mean for n_{ij}) give

$$d(\ln \phi_{ij}{}^{\overline{rep}})/d\ln r = \{(d\ln \phi_i{}^{\overline{rep}}/d\ln r)(d\ln \phi_j{}^{\overline{rep}}/d\ln r)\}^{1/2}$$
(27)

which for the exponential-6 potential can be written as

$$b_{ij}r = (b_i b_j)^{1/2} r \quad .$$
(28)

From Eq. (21) we see that $b = \alpha/r_m$, which implies

$$\frac{\alpha_{ij}}{r_{m_{ij}}} = \left[\frac{\alpha_i \alpha_j}{r_{m_i} r_{m_j}} \right]^{1/2}$$
(29)

or

$$\alpha_{ij} = \gamma(\alpha_i \alpha_j)^{1/2} \quad \text{and} \quad r_{m_{ij}} = \gamma(r_{m_i} r_{m_j})^{1/2}$$
(30)

where γ is to be determined.

Substitution of Eq. (30) into Eq. (22) along with $\sigma_{ij} = (\sigma_i \sigma_j)^{1/2}$ from the previous chapter gives us an equation for γ in terms of known parameters of the pure fluids (i.e., σ_i, r_{m_i}, α_i). Resulting values for γ are near one (Table 5) and thus α_{ij} is nearly the simple geometric mean. Values of unlike-pair parameters for three binary mixtures for which exponential-6 like-pair parameters are available are given in Table 5. These are based on a geometric mean rule for ϵ and σ and Eqs. (30) and (22) for α. The like-pair parameters were taken from Sherwood and Prausnitz.[12] Results of the prediction of the cross-term second virial coefficient with these parameters are given in Table 6.

Conclusions

In two of the three cases the root-mean-square deviations for the exponential-6 potential with the mixture rules proposed are lower than the deviations for the Mie (n,6) potential with the same rules. In the Ar + N_2 mixture the deviation of 1.8 cm^3/mole is greater than 0.6 cm^3/mole found with the Mie (n,6) potential. However, either potential model fits the cross-term second virial coefficient within experimental error with the proposed mixture rules. The predictions of the cross virial coefficient show that mixture rules obtained previously for the Mie (n,6) potential can be extended to the exponential-6 potential.

Table 5. Unlike-pair parameters.

System	ε_{ij}/k (°K)	σ_{ij} (Å)	$r_{m_{ij}}$ (Å)	α_{ij}	γ
CH_4 + Ar	185.14	3.431	3.752	20.77	0.9996
Ar + N_2	156.05	3.373	3.665	23.21	0.9990
CH_4 + CF_4	301.68	3.848	3.983	83.77	0.9872

Table 6. Cross virial coefficient[a] B_{12}.

System	Temperature (°K)	B_{12} (cm³/mole)	
		Experimental	Calculated
CH_4 + Ar	142.6	−138.6	−137.0
	176.7	− 86.7	− 90.7
	239.8	− 48.1	− 47.3
	295.0	− 26.9	− 27.2
	rms dev		2.2
Ar + N_2	148.2	− 81.6	− 79.5
	173.2	− 59.1	− 57.2
	198.2	− 44.0	− 41.7
	223.2	− 32.6	− 30.4
	248.2	− 23.7	− 21.8
	273.2	− 16.4	− 15.0
	298.2	− 10.9	− 9.6
	323.2	− 6.2	− 5.1
	rms dev		1.8
CH_4 + CF_4	273.16	− 62.07	− 59.00
	298.16	− 48.48	− 45.44
	323.16	− 37.36	− 34.48
	348.16	− 28.31	− 25.43
	373.16	− 20.43	− 17.85
	398.16	− 13.98	− 11.39
	423.16	− 8.33	− 5.83
	448.16	− 3.21	− 1.01
	473.16	1.02	3.24
	498.16	4.94	6.98
	523.16	8.28	10.33
	548.16	11.39	13.32
	573.16	14.10	16.02
	598.16	16.55	18.47
	623.16	18.88	20.69
	rms dev		2.30

[a]Experimental data used for comparison are the same as that in Chapter 2.

CHAPTER 4

THE RELATIONSHIP BETWEEN THE MIE (n,6) POTENTIAL AND
EXPONENTIAL-6 POTENTIAL

Introduction

Hanley[2] and Klein[2,1] have recently shown that five of the
common three-parameter pair potentials are essentially equivalent
with respect to the ability to predict the second virial coefficients
of pure gases. It has been shown in the previous chapter that for
two of these potentials, the Mie (n,6) potential

$$\phi(r) = \frac{6\varepsilon}{(n-6)} \{(r_m/r)^n - (n/6)(r_m/r)^6\} \tag{31}$$

and the exponential-6 potential

$$\phi(r) = \frac{6\varepsilon}{(\alpha-6)} \{\exp[\alpha(1-r/r_m)] - (\alpha/6)(r_m/r)^6\} \quad ; \tag{32}$$

though the forms of the repulsive energy differ, a relationship exists
between the parameters of the two potentials. In the (n,6) potential

$$\frac{d \, \ell n \phi^{rep}}{d \, \ell nr} = -n \quad . \tag{33}$$

For the exponential-6 potential

$$\frac{d \, \ell n \phi^{rep}}{d \, \ell nr} = -(\alpha/r_m)r \quad . \tag{34}$$

As n and α approach infinity both potentials become identical to the
Sutherland (∞,6) potential. Thus in this limit the parameters ε and r_m
for the two potentials would be the same when found from fitting the

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same set of second virial coefficient data. This suggests that for large values of n and α the parameters ε, as well as r_m, may have essentially the same value in the two potential models.

Equivalence of Potential Parameters

In Chapter 3 it was pointed out that Eqs. (33) and (34) implied that the quantity α/r_m in the exponential-6 potential should obey the same mixture rule as the parameter n in the (n,6) potential. If, however, it is assumed (a) that the values of r_m in Eqs. (31) and (32) are the same value, (b) that $\phi(r_m)$ by Eq. (31) is equal to $\phi(r_m)$ by Eq. (32) and (c) that $d\ln\phi/d\ln r$ at r_m by Eq. (33) is equal to that by Eq. (34) then the following equivalence of parameters is obtained:

$$\varepsilon_{(n,6)} = \varepsilon_{(exp-6)} \tag{35}$$

$$r_{m_{(n,6)}} = r_{m_{(exp-6)}} \tag{36}$$

$$n_{(n,6)} = \alpha_{(exp-6)} \; . \tag{37}$$

This suggests that where sets of the three-potential parameters are available for one potential they may be used for the three parameters in the other potential model. In order to test this equivalence, exponential-6 parameters for six pure gases, determined by either Sherwood and Prausnitz[12] or Klein[1] from fitting second virial coefficients, have been used with Eqs. (35) to (37) to predict (n,6) potential parameters for the same gases. The results of predicting the second virial coefficients with the (n,6) potential using these parameters are given in Table 7. In general the results are almost within the

Table 7. Second virial coefficients of pure gases predicted
with (n,6) potential using exponential-6 parameters.[a]

Gas	Temperature range (°K)	Number of experimental points	rms dev $(cm^3/mole)$	Data ref.
CF_4	273.16-623.16	15	0.11	b
$C(CH_3)_4$	303.16-548.16	16	2.2	c,d,e
C_2H_6	220.0 -500.0	11	2.4	f
N_2	400.0 -700.0	4	1.4	f
CH_4	273.16-623.16	15	1.61	b
Ar	81.0 -600.0	14	7.7	f

[a]The root mean square (rms) deviations are the deviations between
calculated virial coefficients and the experimental data from the
reference indicated. The experimental data in some cases are not the
same as those used by others for the determination of the exponential-6
parameters in Table 8. However, in all such cases the experimental
data in Table 7 do cover the same temperature range as that used by
the original authors to determine the parameters.

[b]D. R. Douslin, R. H. Harrison, and R. T. Moore, J. Phys. Chem. 71,
3477 (1967).

[c]J. A. Beattie, D. R. Douslin, and S. W. Levine, J. Chem. Phys. 20,
1619 (1952).

[d]S. D. Hamann and J. A. Lambert, Australian, J. Chem. 7, 1 (1954).

[e]S. D. Hamann, J. A. Lambert, and R. B. Thomas, Australian J. Chem. 8,
149 (1955).

[f]J. H. Dymond and E. B. Smith, The Virial Coefficients of Gases
(Clarendon, Oxford, 1969).

experimental uncertainties. As might be expected the worst results

are obtained for argon which has the lowest value of α equal to 18.

The potential parameters used are given in Table 8. These findings,

along with those of Hanley and Klein, indicate that for the second

virial coefficient of most molecules there is little real difference

between the (n,6) and exponential-6 potentials.

Unlike-Pair Parameters

The implied equivalence of the potential energy functions

suggests that the mixture rules for the exponential-6 potential

parameters should be even simpler than those suggested in Chapter 3.

The exponential-6 mixture rules could be taken to be the same as those

for the (n,6) potential in Chapter 2.

$$\epsilon_{ij} = (\epsilon_i \epsilon_j)^{1/2} \tag{38}$$

$$\sigma_{ij} = (\sigma_i \sigma_j)^{1/2} \tag{39}$$

$$\alpha_{ij} = (\alpha_i \alpha_j)^{1/2} \tag{40}$$

These mixture rules have been used with the exponential-6

potential and the parameters in Table 8 to predict the cross-term

second virial coefficients (Table 9) of six binary gas systems previously

studied with the (n,6) potential. The predictions of the rules in

Eqs. (38) to (40) with the exponential-6 potential are similar to those

with the (n,6) potential in Chapter 2. The predictions for the

$C_2H_6 + N_2$ and $CH_4 + C(CH_3)_4$ systems are not as good with the exponential-6

potential as with the (n,6) potential, but they are much better than

Table 8. Exponential-6 potential parameters.[a]

Component	ε/k (°K)	r_m (Å)	α (or n)	Ref.
CF_4	403.6	4.209	300.0	b
$C(CH_3)_4$	635.4	5.980	100.0	b
C_2H_6	377.93	4.502	30.0	c
N_2	160.2	3.695	30.0	b
CH_4	225.5	3.868	24.0	b
Ar	152.0	3.644	18.0	b

---

[a] For the (n,6) potential σ, the value of r where $\phi(r) = 0$, is found from

$$\sigma = r_m \left(\frac{6}{n} \right)^{\frac{1}{n-6}} \quad ;$$

for the exponential-6 potential it is found from numerical solution of Eq. (22) in Chapter 3.

[b] A. E. Sherwood and J. M. Prausnitz, J. Chem. Phys. 41, 429 (1964).

[c] M. Klein, J. Res. Natl. Bur. Std. A70, 259 (1966).

Table 9. Cross-term second virial coefficient.[a]

System	rms dev (cm^3/mole)	
	(exp-6)	(n,6)[b]
CH_4 + Ar	2.2	2.40
CH_4 + C_2H_6	1.24	1.27
CH_4 + CF_4	2.85	2.94
CH_4 + $C(CH_3)_4$	7.42	4.2
N_2 + Ar	1.88	0.6
N_2 + C_2H_6	4.71	3.6

[a]Cross-term second virial coefficient data used are identical with those in Chapter 2.

[b]Previously reported in Chapter 2.

the predictions of the (12,6) potential with any of the eleven sets of mixture rules tested by Good and Hope.[8]

It should be pointed out that for a given set of ε, r_m, n (or α) the value of $\sigma_{(n,6)}$ does not equal to $\sigma_{(exp-6)}$. A given mixture is characterized by ε_i, ε_j, r_{m_i}, r_{m_j} and n_i, n_j (or equivalently α_i and α_j). Using Eq. (39) for the exponential-6 potential and for the (n,6) potential does not lead to the same $r_{m_{ij}}$ for both potentials. This result is, of course, inconsistent with Eq. (36). It would have been consistent if the following,

$$\sigma_{(n,6)} = \sigma_{(exp-6)} \tag{41}$$

were chosen in place of Eq. (36). This choice could have been made in the first place. In fact, calculations based on Eqs. (35), (37) and (41) give about the same results as reported in Table 7. This indicates that the effect of the inconsistency referred to above is small. To further illustrate this fact the case of the $CH_4 + C(CH_3)_4$ system is examined. The pure component parameters for this system are given in Table 8. If these are taken to be (n,6) parameters, the rules in Eqs. (38) to (40) would predict $r_{m_{ij}} = 4.787$ Å. If taken to be exponential-6 parameters, the same rules predict $r_{m_{ij}} = 4.782$ Å. This difference would lead to a difference of only 0.3% in the predicted virial coefficients.

Conclusions

The (n,6) and exponential-6 potentials are sufficiently alike with respect to the prediction of second virial coefficients that

sets of the three exponential-6 parameters can be used for the three

parameters in the (n,6) potential with very good results in the

prediction of second virial coefficients. The mixture rules shown

previously to work with the (n,6) potential give similar results with

the exponential-6 potential.

CHAPTER 5

SATURATED LIQUID PROPERTIES FROM THE
MIE (n,6) POTENTIAL

Introduction

The ability of the perturbation theory of liquids developed by
Barker and Henderson[14] to reproduce liquid properties calculated by
means of Monte Carlo or molecular dynamics makes this theory an excellent
tool for studying pair potential energy functions for liquids. Hanley
and Klein[1,2] have recently shown that various three-parameter potentials
(Kihara, Mie (n,6), exponential-6 and Morse potentials) are equivalent
with respect to their ability to reproduce experimental second virial
coefficients and transport properties of gases. However, the Mie (n,6)
potential is of special interest for mixture property calculations
because simple mixture rules have been found (Chapter 2) for the three
parameters (ε/k, σ, n) which accurately reproduce cross-term second
virial coefficients for a wide variety of gaseous mixtures. To our
knowledge the only Mie (n,6) potentials that have been studied by
Monte Carlo methods to any extent for the liquid are the (12,6) and
(18,6) potentials for liquid argon.[14,15] The Lennard-Jones (12,6)
potential with the parameters ε/k and σ determined by Michels et al.[16]
performs remarkably well (better than that of Hanley and Klein) for
liquid argon as demonstrated by Monte Carlo[15] and perturbation theory[14]
calculations. The effect of the source of potential parameters is
demonstrated for argon and methane by using two empirical sets of
(12,6) potential parameters for each of these liquids in perturbation
theory (see Table 12). Corrections for nonadditivity of pair potentials

have not been included; thus to the extent that many-body interactions are important the (n,6) potentials should be regarded as _effective_ pair potentials.

The Mie (n,6) potential is of the form

$$\phi(r) = \kappa \, \epsilon \left[\left(\frac{\sigma}{r} \right)^n - \left(\frac{\sigma}{r} \right)^6 \right] \tag{42}$$

where

$$\kappa = \left(\frac{1}{n-6} \right) \left(\frac{n^n}{6^6} \right)^{\frac{1}{n-6}} . \tag{43}$$

Barker-Henderson Perturbation Theory

The expression for the residual free energy is derived by Barker and Henderson and is given by

$$A^r/NkT = A_o^r/NkT + A_1^* + A_2^* + A_3^* \tag{44}$$

where

$$A_1^* = 2\pi\rho\beta \int_\sigma^\infty g_o(r)\phi(r)r^2 dr \tag{45}$$

$$A_2^* = -\pi\rho\beta \left(\frac{\partial\rho}{\partial P} \right)_o \int_\sigma^\infty g_o(r)\phi^2(r)r^2 dr \tag{46}$$

$$A_3^* = -\pi\rho^2\beta \left(\frac{\partial\rho}{\partial P} \right)_o \int_\sigma^\infty \frac{\partial g_o}{\partial\rho} \phi^2(r)r^2 dr \tag{47}$$

and A_o^r, $g_o(r)$ and $(\partial\rho/\partial P)_o$ are the residual Helmholtz free energy, radial distribution function and compressibility, respectively, of a hard-sphere reference fluid with diameter $\underset{\sim}{d}$ defined by

$$\underset{\sim}{d}^* = \underset{\sim}{d}/\sigma = \int_0^1 [1 - \exp(-\beta\phi)]d(r/\sigma) \tag{48}$$

where σ is the distance parameter in the pair potential and $\beta = (kT)^{-1}$.

The second order term $(A_2^* + A_3^*)$ is derived from the local compressibility approximation of Barker and Henderson.[14] This is the approximation adopted for this study.

The residual internal energy, U^r, is obtained by numerical differentiation of the residual Helmholtz free energy according to the following equation

$$U^r/NkT = -T \, \partial(A^r/NkT)/\partial T \quad . \tag{49}$$

The residual entropy is calculated from the relation

$$S^r/Nk = (U^r/NkT - A^r/NkT) \quad . \tag{50}$$

The numerical integrations were performed using a Gaussian integration routine. Percus-Yevick hard-sphere radial distribution functions were used for $g_o(r)$. These functions were chosen because they yield accurate values for the first order term in the Helmholtz free energy when compared with Monte Carlo calculations.[17] Carnahan and Starling's expressions[18] were used for hard-sphere pressure, compressibility and free energy. Analytical expressions were utilized to generate the radial distribution function[17,19] and its density derivative (Appendix B).

McDonald and Singer[15] have computed internal energies and pressures for the (18,6) pair potential using the Monte Carlo method at three different state points. At these state points pressures and

internal energies were recalculated using the (12,6) and the (18,6)
pair potentials in the Barker-Henderson perturbation theory. The
results are compared in Table 10. In the case of the (12,6) potential
the agreement for energies and pressures is excellent. For the (18,6)
potential the energies compare well with Monte Carlo values. The
pressures do not compare as well as do those for the (12,6) potential.
The Monte Carlo and the perturbation theory pressures are both negative
values. However, it is important to note that while the state points
were the same for both pair potentials, the reduced temperatures for
the (18,6) potential were considerably lower than those for the (12,6)
potential. The differences in Monte Carlo and perturbation theory
pressures may well be due to slow convergence of perturbation theory
at low reduced temperatures.

Liquid Properties from Best Virial Coefficient (n,6) potential

Mie (n,6) potential functions for this study were selected from
the tables of Klein.[1] For each substance the (n,6) potential parameters
n, ϵ/k and σ which best fit the experimental second virial coefficient
were chosen. Klein has determined parameters for CF_4 only for
potentials with n up to 40. An optimal set of parameters for CF_4 with
n = 136.3 was determined in Chapter 2. The best parameters for each
substance studied are given in Table 11 along with the (12,6) parameters
determined by Klein. In general the properties (residual energies and
entropies) along the saturation curve (Table 12) calculated using the
best gas potentials in Table 11 agree better with experimental data than

Table 10. Comparison between Monte Carlo
calculations and perturbation
theory.

T (°K)	V (cm^3/mole)	(12,6) Potential[d]			(18,6) Potential[e]		
		a	b	c	a	b	c
				$-U^r$ (cal/mole)			
97.0	26.90	1480	1424	1420	1566	1501	1517
108.0	28.48	1387	1352	1351	1457	1410	1427
136.0	32.52	1192	1186	1189	1233	1214	1233
				P (atm)			
97.0	26.90	609	663	660	−519	−278	−273
108.0	28.48	443	499	498	−415	−225	−224
136.0	32.52	289	351	351	−113	− 53	− 58

[a] Monte Carlo calculations.[15]

[b] Macroscopic compressibility approximation and perturbation theory.

[c] Local compressibility approximation and perturbation theory.

[d] Parameters from Michels et al.[16] ε/k = 119.8 K, σ = 3.405 Å .

[e] Parameters from Dymond et al.[20] ε/k = 160.3 K, σ = 3.277 Å .

Table 11. (n,6) Potential energy parameters[a]
from second virial coefficients.

Molecule	n	ϵ/k (°K)	σ (Å)
Argon[b]	12	119.8	3.405
Argon	12	115.06	3.515
Argon[c]	13	123.99	3.458
Argon	16	147.50	3.315
Nitrogen	12	94.77	3.804
Nitrogen	16	118.12	3.650
Nitrogen	24	148.59	3.491
Methane	12	143.25	4.056
Methane[d]	12	148.63	3.775
Methane	17	189.17	3.779
Methane	27	244.71	3.519
Perfluoromethane	12	151.90	4.742
Perfluoromethane	30	260.33	4.378
Perfluoromethane[e]	136.3	373.31	4.186

[a]Except where otherwise specified potential parameters are those of Hanley and Klein.[1,2]

[b]Michels' parameters.[16]

[c]Parameters determined for this work.

[d]Parameters obtained from Michels' argon parameters as follows

$$\epsilon/k_{CH_4} = 119.8 \ (T_{B_{CH_4}}/T_{B_{Ar}}) \text{ and } \sigma_{CH_4} = 3.405 \ (V_{B_{CH_4}}/V_{B_{Ar}})^{1/3}, \text{ where}$$

T_B and V_B are Boyle temperature and Boyle volume, respectively, taken from D. R. Douslin, R. H. Harrison, and R. T. Moore, J. Phys. Chem. 71, 3477 (1967).

[e]Parameters from Chapter 4.

Table 12. Saturated liquid properties.

Argon

T (°K)	Experimental	Potential			
		$(12,6)^b$	$(12,6)^c$	$(13,6)$	$(16,6)^a$

Residual Energy ($-U^r/NkT$)

T (°K)	Experimental	$(12,6)^b$	$(12,6)^c$	$(13,6)$	$(16,6)^a$
83.81	8.52	8.34	8.49	8.64	8.77
87.29	8.05	7.87	8.03	8.16	8.26
90.0	7.70	7.53	7.70	7.82	8.00
95.0	7.08	6.97	7.14	7.24	7.29
100.0	6.53	6.46	6.63	6.71	6.73
110.0	5.52	5.58	5.72	5.78	5.76
120.0	4.68	4.76	4.92	4.95	4.90
130.0	3.93	4.01	4.16	4.17	4.11
140.0	3.22	3.29	3.43	3.42	3.35
150.86	1.91	1.76	1.84	1.83	1.77

Residual Entropy ($-S^r/Nk$)

T (°K)	Experimental	$(12,6)^b$	$(12,6)^c$	$(13,6)$	$(16,6)^a$
83.81	3.59	3.47	4.05	3.82	3.33
87.29	3.45	3.34	3.89	3.67	3.21
90.0	3.34	3.24	3.77	3.57	3.12
95.0	3.14	3.09	3.58	3.40	2.97
100.0	2.95	2.93	3.39	3.21	2.81
110.0	2.59	2.63	3.02	2.88	2.53
120.0	2.29	2.32	2.65	2.57	2.24
130.0	1.97	2.00	2.25	2.16	1.94
140.0	1.65	1.64	1.86	1.78	1.62
150.86	0.97	0.82	0.90	0.88	0.82
Pressures	pos.	pos.	pos.	pos.	neg.

Methane

T (°K)	Experimental	Potential			
		$(12,6)^d$	$(12,6)$	$(17,6)$	$(27,6)^a$

Residual Energy ($-U^r/NkT$)

T (°K)	Experimental	$(12,6)^d$	$(12,6)$	$(17,6)$	$(27,6)^a$
90.66	10.61	10.29	10.59	11.89	11.67
95.0	9.96	9.65	10.05	11.13	10.86
100.0	9.32	9.01	9.47	10.38	10.08
105.0	8.73	8.44	8.94	9.72	9.38
110.0	8.18	7.92	8.45	9.10	8.75
111.66	7.99	7.76	8.30	8.91	8.55
120.0	7.19	7.00	7.58	8.01	7.64
130.0	6.34	6.21	6.81	7.09	6.71

Table 12 (Continued)

T (°K)	Experimental	(12,6)[d]	(12,6)	(17,6)	(27,6)[a]
Residual Entropy ($-S^r/Nk$)					
100.0	3.75	3.80	5.77	4.24	3.41
105.0	3.58	3.65	5.48	4.08	3.26
110.0	3.44	3.51	5.22	3.90	3.13
111.66	3.40	3.46	5.15	3.85	3.07
120.0	3.16	3.23	4.74	3.58	2.87
130.0	2.86	2.97	4.28	3.29	2.64
Pressures	pos.	pos.	pos.	pos.	neg.

Nitrogen

		Potential		
T (°K)	Experimental	(12,6)	(16,6)	(24,6)[a]
Residual Energy ($-U^r/NkT$)				
63.18	10.62	9.86	10.61	10.93
65.0	10.21	9.52	10.22	10.49
70.0	9.11	8.66	9.23	9.42
75.0	8.18	7.90	8.36	8.48
77.35	7.81	7.58	8.00	8.11
80.0	7.41	7.25	7.61	7.70
90.0	6.11	6.10	6.32	6.33
100.0	5.06	5.10	5.23	5.18
110.0	4.12	4.22	4.26	4.19
Residual Entropy ($-S^r/Nk$)				
63.18	4.30	5.07	4.38	3.86
65.0	4.19	4.94	4.28	3.77
70.0	3.90	4.60	4.00	3.49
75.0	3.63	4.27	3.74	3.29
77.35	3.50	4.15	3.64	3.20
80.0	3.37	4.01	3.51	3.10
90.0	2.97	3.46	3.06	2.72
100.0	2.63	2.92	2.63	2.35
110.0	2.20	2.43	2.20	2.00
Pressures	pos.	pos.	pos.	neg.

Table 12 (Continued)

Perfluoromethane

T (°K)	Experimental	Potential		
		(12,6)	(30,6)	(136.3,6)[a]

Residual Energy, $(U^r - U^r_{116.49°})/NkT$

116.49	0	0	0	0
127.60	0.39	-0.15	0.38	0.57
144.27	1.01	-0.23	0.86	1.22
166.49	1.88	-0.21	1.39	1.89
194.27	2.56	0.03	2.03	2.60
224.83	3.62	0.93	3.24	3.82
227.66	4.44	1.80	4.20	4.77

Residual Entropy, $(S^r - S^r_{116.49°})/Nk$

116.49	0	0	0	0
127.60	0.37	0.81	0.44	0.40
144.27	1.03	1.85	1.04	0.89
166.49	2.00	3.02	1.73	1.47
194.27	2.92	4.34	2.61	2.17
224.83	4.00	6.10	3.89	3.23
227.66	4.65	6.92	4.56	3.82

Pressures	pos.	pos.	pos.	neg.

---

[a]Best gas potential.

[b]Michels' parameters.

[c]Hanley and Klein's parameters.

[d]Parameters estimated from Michels' argon parameters and corresponding states (see Table 11).

do those calculated using the (12,6) potential. However, the pressures predicted by the best gas potentials were all negative along the saturation curve. Experimental densities were used in the calculations at all temperatures. Results for CF_4 only are given in Figure 1.

(n,6) Potentials for Liquids

The effect on the calculated properties of varying the value of n was studied. For each n the second virial coefficient potential parameters of Klein[1] were used except for the (13,6) potential parameters for argon. Klein has not reported parameters for the (13,6) potential. These parameters have been determined for this work using the same second virial coefficient data used by Klein. The residual energies and residual entropies were calculated using these potentials in order to find which one of them best predicts these liquid properties. For all molecules examined it was found that one of the values of n between 12 and the best n for virial coefficients gave the best agreement between predicted and experimental liquid properties. The results are tabulated in Table 12. Experimental densities were again used at all temperatures. Results for CF_4 are given in Figure 1. For these intermediate n-values all pressures calculated along the saturation curve were positive. In fact in every case it was found that the best n for the prediction of liquid residual energy and entropy was the highest value of n which still predicted positive pressures. This observation suggests that an excellent estimate for n to be used for the liquid could be obtained by merely choosing the (n,6) potential which correctly predicted some experimental liquid density using ϵ/k and σ obtained from a fit of the second virial coefficient.
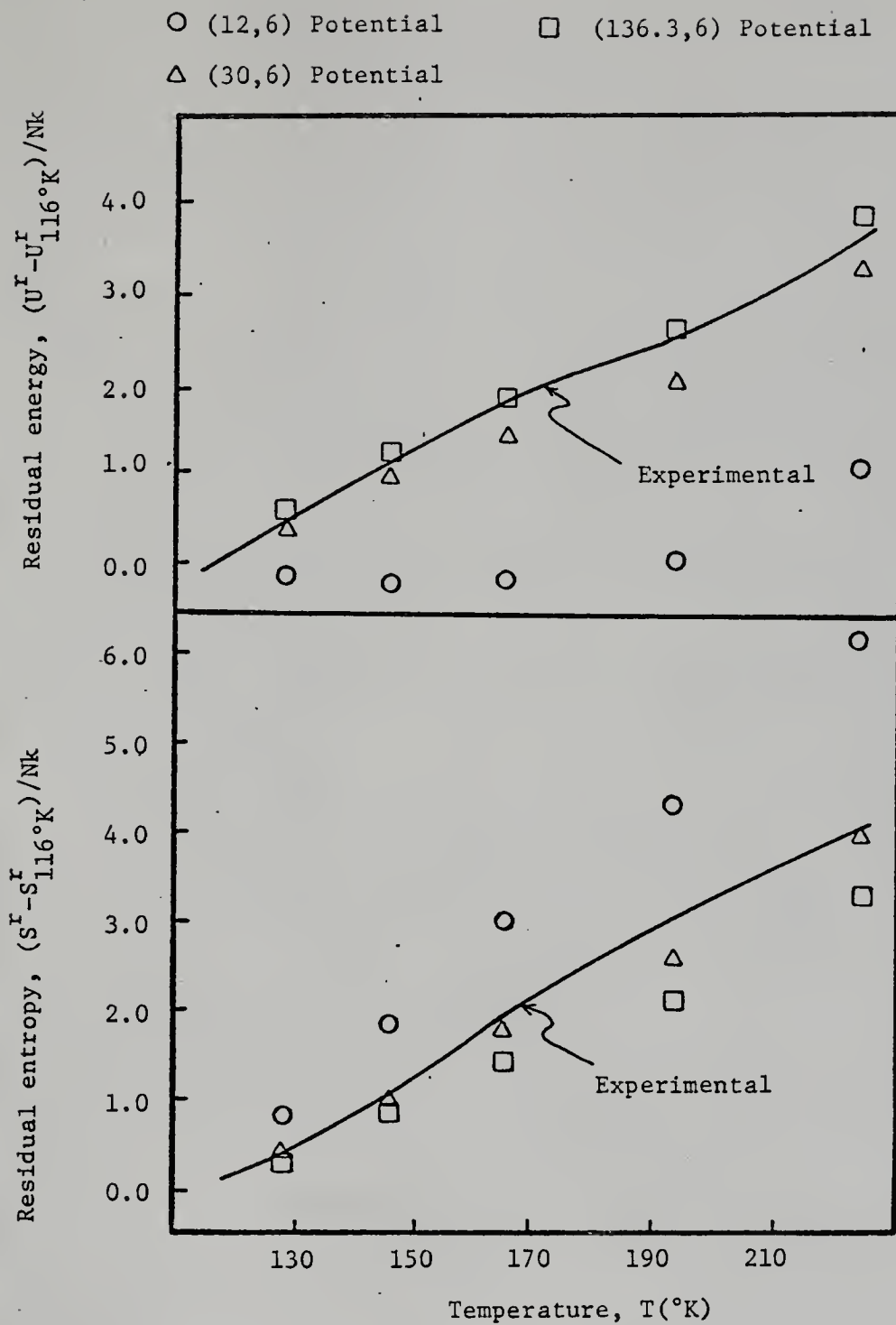
Figure 1. Residual properties of liquid CF_4.

Conclusions

The Barker-Henderson perturbation theory using the (18,6) potential function agrees with Monte Carlo calculations of McDonald and Singer using the same potential. Barker and Henderson have previously shown the excellent agreement between perturbation theory and Monte Carlo calculations for the (12,6) potential. It is reasonable to assume that other (n,6) potentials can be utilized in perturbation theory to yield thermodynamic properties of pairwise additive fluids.

The best (n,6) potentials obtained by Klein for second virial coefficients yield residual properties that agree better with experimental data than do those calculated with Klein's (12,6) potential.

For the systems studied (argon, nitrogen, methane, and perfluoromethane) (n,6) potentials were found which give better computed values for the residual properties along the saturated liquid curve when compared to the properties computed with virial coefficient potentials. The results suggest that it may be possible to obtain a suitable value of n for the liquid using only one experimental P,V,T point for the liquid in addition to the gas phase second virial coefficient data.

CHAPTER 6

EXCESS PROPERTIES OF THE METHANE-PERFLUOROMETHANE SYSTEM
FROM THE ONE-FLUID VAN DER WAALS PRESCRIPTION
IN PERTURBATION THEORY

Introduction

Theories of liquid mixtures are usually based either on two-parameter corresponding states with one of the mixture components taken as the reference substance,[21,22] or on theories of the liquid state which employ a two-parameter pair potential.[23,24] Common to most of these theories is an adjustable parameter ξ which takes into account the deviation of the unlike-pair energy parameter ε_{ij} from the geometric mean of the two like-pair energy parameters. For molecules which differ greatly in character the factor ξ is usually significantly less than 1.0, e.g., $\xi = 0.909$ for the $CH_4 + CF_4$ interaction, when the same pair potential or reference fluid is used for both molecules in a binary mixture. It has been shown (Chapter 5) that methane and perfluoromethane obey different $(n,6)$ pair potentials and these potentials are not the same ones for gas and liquid phases. It is the purpose of this chapter to demonstrate the importance of taking into account the different pair potentials of CH_4 and CF_4 in predicting the thermodynamic properties of gas and liquid mixtures of these molecules.

One-Fluid Perturbation Theory of Mixtures

The theory chosen for the present study is the one-fluid theory of mixtures with van der Waals prescription for the mixture potential

energy parameters.

$$\epsilon_m \sigma_m^3 = \left[x_1^2 \epsilon_1 \sigma_1^3 + 2x_1 x_2 \epsilon_{12} \sigma_{12}^3 + x_2^2 \epsilon_2 \sigma_2^3 \right] \qquad (51)$$

$$\sigma_m = \left[x_1^2 \sigma_1^3 + 2x_1 x_2 \sigma_{12}^3 + x_2^2 \sigma_2^3 \right]^{1/3} \qquad (52)$$

The perturbation theory of Barker and Henderson[14] was used to calculate

the properties of the pure liquids and liquid mixtures reported herein

(see Appendix C) using the respective potential energy functions and

parameters. Except where otherwise noted calculations were made with

first order perturbation theory. Carrying out the calculations to

second order does not significantly change the values of the predicted

excess properties.

Leonard et al.[23] have presented a comparison of the one-fluid

theory using van der Waals prescription with both (12,6) Monte Carlo

calculations and the multicomponent version of perturbation theory.

Their results show the van der Waals predictions to be as good as or

better than those obtained with the multicomponent perturbation theory.

As noted by Leonard et al. the van der Waals results are not based on

the (12,6) potential as are the Monte Carlo and perturbation results.

Calculations have been made with the one-fluid van der Waals prescription

using the (12,6) potential in perturbation theory. These calculations,

reported in Table 13 for one temperature and composition, give a better

comparison of the van der Waals theory with other (12,6) theories of

mixtures than results reported by Leonard et al.[23] The one-fluid

van der Waals prescription in perturbation theory predicts an excess

Table 13. Comparison of one-fluid van der Waals
model with Monte Carlo and multicomponent
perturbation theory calculations.

$T = 115.8°K$, $P = 0$ and $x_1 = x_2 = 0.5$, $\epsilon_1/k = 119.8°K$,

$\epsilon_2/k = 167.0°K$, $\sigma_1 = 3.405$ Å, $\sigma_2 = 3.633$ Å, $\epsilon_{12} = (\epsilon_1\epsilon_2)^{1/2}$,

$\sigma_{12} = (\sigma_1 + \sigma_2)/2$.

Theory	G^E (J/mole)	V^E (cm^3/mole)
Monte Carlo[a]	34 ± 10	−0.54 ± .20
Multicomp. Pert.[b]	32.7	−0.73
vdW[c]	42.2	−0.79
vdW[d]	38.1	−0.70
vdW[e]	36.7	−0.63

[a]McDonald's Monte Carlo calculations reported by Leonard et al.[23]

[b]Taken from ref. (23).

[c]Reported by Leonard et al.[23] Not based on (12,6) potential.

[d]Calculated from vdW prescription in second order perturbation theory.
Macroscopic compressibility approximation to second order contribution
to free energy was used.[14]

[e]Calculated from vdW prescription in first order perturbation theory.

volume and excess free energy almost the same as multicomponent perturbation theory and within the estimated uncertainty of the Monte Carlo results.

The Methane-Perfluoromethane System

Earlier calculations for liquid mixtures in this system have been made under the assumption that all pair interactions follow the same pair potential model, usually the (12,6) potential. In all such calculations it is found that it is necessary to employ an empirical factor ξ multiplying the geometric mean of the like-pair energy parameters. Heretofore ξ has been determined from binary mixture data. For the methane + perfluoromethane system the value of ξ required to fit either cross-term second virial coefficient data or excess properties of liquid mixtures is significantly less than 1.0 (approximately 0.91) for the 12,6 potential.

It has been demonstrated (Chapter 2) for cross-term second virial coefficients that when the two like-pair interactions in binary systems are allowed to obey different (n,6) potentials, the unlike-pair potential parameters are all the simple geometric mean of the like-pair parameters. This observation eliminates the need for binary data in gas mixture calculations. In order to determine whether these findings are useful for predicting liquid mixture properties, the gas phase potential energy functions have been used to predict a value for ξ. This ξ is then used to calculate liquid mixture properties with a theory which requires the use of the same pair potential for all intermolecular interactions. Such a theory is the one-fluid theory with

van der Waals prescription for the mixture potential parameters. The unlike-pair parameters ϵ_{ij} and σ_{ij} are calculated for any one reference potential chosen to represent all intermolecular interactions.

The method used to estimate these parameters makes use of properties of the second virial coefficient at the Boyle temperature. The Boyle temperature T_B is defined as the temperature at which the second virial coefficient $B(T)$ is equal to zero. The Boyle volume V_B is defined in the usual way, namely,

$$V_B = T_B (dB(T)/dT)_{T_B} . \tag{53}$$

When two species (i and j) obey the same pair potential energy function their potential parameters are related as follows:

$$(\epsilon/k)_i / (\epsilon/k)_j = T_{B_i} / T_{B_j} \tag{54}$$

$$\sigma_i / \sigma_j = (V_{B_i} / V_{B_j})^{1/3} . \tag{55}$$

Eqs. (54) and (55) are not exact if the two molecules do not obey the same pair potential. Eqs. (54) and (55) provide a means of estimating the parameters of one molecule from those of another when both are to be represented by the same potential energy function, e.g., the (12,6) potential.

Douslin et al.[25] have shown that the second virial coefficients of pure CH_4 and CF_4 as well as the cross-term second virial coefficients of the $CH_4 + CF_4$ pair all fall very nearly on one reduced curve provided the reducing parameter for the temperature is T_B and that for the second virial coefficient is V_B. This correlation is followed in spite of

the fact that all three sets of virial coefficient data obey different pair potentials as shown in Chapter 2. This near coincidence suggests that Eqs. (54) and (55) will be good estimates for the parameter ratios. Eqs. (54) and (55) are commonly employed with the experimental like- and unlike-pair Boyle temperatures and Boyle volumes to predict the (12,6) parameters for $CF_4 + CF_4$ and $CH_4 + CF_4$ from those of $CH_4 + CH_4$. Methane is usually taken as the reference fluid for these mixture calculations.

In part of this work the experimental Boyle properties have not been used. Instead the (n,6) gas phase potential energy functions and the proposed mixture rules of Chapter 2 have been used with the series expression[26] for the (n,6) second virial coefficient to calculate what are presumably good estimates of the experimental Boyle properties. The gas phase potential energy parameters for the (n,6) potential are listed in Table 14 for the like and unlike pair. Each of the unlike-pair parameters is the geometric mean of the respective like-pair parameters. This set of parameters fits the experimental cross-term second virial coefficient for the $CH_4 + CF_4$ system in the temperature range 273.16 to 623.16°K with a root-mean-square deviation of 1.20 cm^3/mole.

Using the Boyle temperatures and volumes estimated by the potentials in Table 14 with CH_4 as the reference fluid, the ratios f and g in Table 15 were calculated from Eqs. (54) and (55). These ratios are independent of the pair potential chosen for the reference liquid. Parameters obtained from these ratios are for the same potential as that of the reference liquid.

It can be seen from Table 15 that the predicted $\xi = \epsilon_{ij}/(\epsilon_i \epsilon_j)^{1/2}$ is 0.91688 and results entirely from forcing all of the molecular

Table 14. Gas phase potential parameters.

Molecular Pair	ε/k (°K)	σ (Å)	n	Reference
$CH_4 + CH_4$	218.00	3.568	21.00	3
$CF_4 + CF_4$	373.31	4.186	136.30	Chapter 2
$CH_4 + CF_4$	285.27	3.865	53.50	–

Table 15.[a] Predicted and experimental potential
parameter ratios.

Molecular Pair	$f_i = \epsilon_i/\epsilon_{ref} = T_{B_i}/T_{B_{ref}}$	$g_i = \sigma_i/\sigma_{ref} = (V_{B_i}/V_{B_{ref}})^{1/3}$
$CH_4 + CH_4$	1.000 (1.000)	1.000 (1.000)
$CF_4 + CF_4$	1.0127 (1.017)	1.245 (1.242)
$CH_4 + CF_4$	0.92266 (0.917)	1.130 (1.132)

[a]Values in parentheses were determined from the experimental Boyle
properties given in reference (25) and used for calculations in
references (21) and (23).

interactions to obey the same potential (as yet unspecified), since this value was predicted on the basis of $\xi = 1.0$ for the gas phase potentials. Parameters obtained from both the predicted and experimental ratios (in parentheses) in Table 15 have been used in the one-fluid perturbation theory with van der Waals prescription for the mixture parameters (hereafter referred to as the vdW perturbation model) to predict the excess properties of the equimolar $CH_4 + CF_4$ mixture at 111°K.

The effect on predicted properties of the choice of reference fluid, source of potential energy parameters, and choice of the potential energy function of the reference fluid has been studied. Results for the (12,6) potential with CH_4 as the reference fluid are given in Table 16 along with the results obtained by Leland et al.[21] and Leonard et al.[23] for the same system with their respective theories and experimental ratios f and g from Table 15. Also included are the one-fluid perturbation results for $\xi = 1.0$ and $\sigma_{ij} = (\sigma_i + \sigma_j)/2$ with the (12,6) potential.

The excess properties predicted by the vdW perturbation model (Table 16) using the experimental f and g from Table 15 and the (12,6) potential are nearly the same as the predictions of the Leland, Rowlinson and Sather theory with experimental f and g. The predictions of the vdW perturbation model are far superior to the Leonard, Barker and Henderson multicomponent perturbation theory predictions for the $CH_4 + CF_4$ system. The apparent failure of the multicomponent perturbation theory for this system may be due to the usual assumption in perturbation theory calculations that the unlike-pair hard-sphere diameter is the arithmetic mean of the two like-pair diameters. It is significant that this

Table 16. Excess properties of the CH_4 + CF_4
mixture at 111°K, P = 0, x_1 = x_2 = 0.5,
with (12,6) potential.

	V^E (cm^3/mole)	G^E (J/mole)
Experimental Data[a]	0.845	360
vdW Perturbation Model (predicted f and g)		
M. Klein CH_4 parameters[b] (1st order theory)	0.89	209
M. Klein CH_4 parameters[b] (2nd order theory)	0.97	213
Sherwood and Prausnitz CH_4 parameters[c]	0.64	224
Leland, Rowlinson and Sather[d] with experimental f and g	0.90	279
Leonard, Barker and Henderson[e] with experimental f and g	-0.97	209
vdW Perturbation Model (experimental f and g)		
Sherwood and Prausnitz CH_4 parameters[c]	1.05	296
vdW Perturbation Model (ξ = 1.0, σ_{ij} = (σ_i + σ_j)/2)		
Sherwood and Prausnitz CH_4 parameters[c]	-0.79	5

[a]Taken from reference 27.

[b]Parameters taken from reference 1.

[c]Parameters taken from reference 12.

[d]Taken from reference 21.

[e]Taken from reference 23.

assumption makes the unlike-pair hard-sphere radial distribution function independent of the mixture rules for the potential energy parameters.

The use of the predicted f and g in the vdW perturbation model with the (12,6) potential yields estimates of the excess properties comparable to the results obtained with experimental f and g although the excess free energy in the former case is somewhat lower. When values calculated with the predicted f and g are compared to those obtained under the assumption $\xi = 1.0$ and $\sigma_{12} = (\sigma_1 + \sigma_2)/2$ in the liquid mixture it is seen that most of the required deviation of ξ from 1.0 is accounted for by the predicted values. The success of these values obtained from the Boyle point correlation on the basis of $\xi = 1.0$ in the gas phase demonstrates that much of the deviation of ξ from 1.0 usually observed in gas and liquid mixture calculations for this system results from the artificial requirement that all pair interactions in the mixture obey the same pair potential model.

The dependence of the predictions on the source of potential parameters is seen from Table 16 by comparing the predicted excess properties using Klein (12,6) CH_4 parameters with those using Sherwood and Prausnitz CH_4 parameters. Table 17 illustrates the effect of varying the reference fluid and the potential energy function on the predictions of the vdW perturbation model. With the experimentally determined f and g excess volumes vary from 0.50 to 1.05 cm^3/mole and excess free energies vary from 296 to 746 J/mole. The highest value for the excess free energy is the least reliable as it occurs with the (136.3,6) potential for which reduced liquid densities are so large

Table 17. Excess properties of the CH_4 + CF_4 mixture at 111°K, $P = 0$, $x_1 = x_2 = 0.5$ with various potentials and reference liquids.

Potential	Ref. Liquid	Source for Parameters	V^E (cm^3/mole)	G^E (J/mole)
Predicted f and g				
12,6	CH_4	1	0.89	209
12,6	CH_4	12	0.64	224
12,6	CF_4	1	0.63	227
12,6	CF_4	12	0.59	226
Experimental f and g				
12,6	CH_4	12	1.05	296
30,6	CF_4	1	0.50	412
21,6	CH_4	3	0.59	350
136.3,6	CF_4	Chapter 2	0.61	746
$\xi = 1.0$, $\sigma_{12} = (\sigma_1 + \sigma_2)/2$				
12,6	CH_4	12	-0.79	5

that the Percus-Yevick hard-sphere radial distribution functions used in the calculations are not accurate.

The dependence of the results on the potential energy function and the reference fluid limits the ability to discriminate between possible mixture rules which might be proposed for parameters. In fact, when one examines the wide variations in the predictions for the actual volumes and residual free energies of a particular pure component or of the mixture using the various potentials and reference systems, it is remarkable that the excess properties are as insensitive as they are to the choice of pair potentials. Some examples of the properties predicted for the liquids are presented in Table 18.

It would appear from the above results that while two-parameter theories of liquid mixtures may hold promise in predicting excess properties of liquid mixtures there is little hope of predicting the actual magnitude of the properties of mixtures and pure liquids with a single pair potential. There is consequently considerable incentive for development of useful theories, such as the Leonard, Barker, Henderson multicomponent perturbation theory,[23] which allow the use of different pair potentials for the constituent molecules. Rogers and Prausnitz[24] have recently used the Leonard, Barker, Henderson theory with the three-parameter Kihara potential with considerable success to predict the magnitudes of both pure and mixed liquid properties for the argon + neopentane and methane + neopentane systems with an empirically adjusted ξ. The values obtained for ξ are 0.994 and 0.988, respectively, when the Kihara potential is used for the liquid state. These values of ξ, which are not far from 1.0, further support

Table 18.   Calculated properties of liquids at 111°K, P = 0.

All results are for first order perturbation theory with experimental f and g. Volumes (V) are in cm^3/mole, and residual Gibbs free energy (G^r) is in J/mole.

Potential[a]	Ref. Liquid	CH_4		CF_4		Equimolar mixture	
		V	G^r	V	G^r	V	G^r
$(12,6)^{13}$	CH_4	39.74	−3839	75.58	− 3958	58.71	−3589
$(30,6)^{12}$	CF_4	27.32	−5914	52.08	− 6095	40.20	−5534
$(136.3,6)^2$	CF_4	19.22	−9716	36.63	−10027	28.23	−9068
Exptl. Data[b]		37.70	−	49.47	−	44.43	−

[a] Superscripts indicate references for potential energy function parameters.
[b] Calculated from data of Croll and Scott.[27]

the conclusion reached in this work that much of the deviation of the
observed ξ from 1.0 that is usually observed results from the use of the
same two-parameter potential for all intermolecular interactions in the
mixture. The value of ξ obtained empirically to fit the cross-term
second virial coefficient in the methane + neopentane system with the
(12,6) potential is approximately 0.93.[28] This value is much lower
than that found by Rogers and Prausnitz for the liquid state using a
three-parameter potential. The cross-term second virial coefficient
for this system has been successfully predicted assuming $\xi = 1.0$ with
the three-parameter (n,6) potential in Chapter 2.

Potential Parameters Independent of Choice of Reference Fluid

As demonstrated previously the predictions of the vdW per-
turbation model are dependent on the choice of the reference fluid and
the particular set of potential energy parameters chosen for that
fluid. Both of these arbitrary choices can be avoided when the gas
phase (n,6) potential energy functions are known for the like- and
unlike-pair interactions. This is accomplished by utilizing Eqs. (56)
and (57). Given two different (n,6) potentials representing the same
molecule, say $(n_1,6)$ and $(n_2,6)$, the following relationship can be
used to estimate the parameters of the $(n_1,6)$ potential from those of
the $(n_2,6)$ potential:

$$(\varepsilon/k)_{n_1} = (\varepsilon/k)_{n_2} (T_B^*)_{n_2} / (T_B^*)_{n_1} \tag{56}$$

$$\sigma_{n_1} = \sigma_{n_2} \{ (V_B^*)_{n_2} / (V_B^*)_{n_1} \}^{1/3} \tag{57}$$

where $T_B^* = T_B / (\varepsilon/k)$ and $V_B^* = V_B / (N\sigma^3)$.

Thus, if the $(n_1,6)$ potential is chosen to represent all interactions in the liquid mixture, and the known gas phase potential for a given interaction is the $(n_2,6)$ potential, then the $(n_1,6)$ parameters can be estimated. From the gas phase potential parameters in Table 14 the liquid phase parameters have been calculated by Eqs. (56) and (57) for all three pair interactions in a given potential. Of course these parameters will be in the ratios given as the predicted ratios in Table 15. Since only one set of parameters results for each potential model chosen, the choice of a reference system does not arise. Parameters for the (12,6) and (30,6) potentials have been determined in this manner and used to predict the excess properties of the $CH_4 + CF_4$ mixture. Results are given in Table 19. The predicted excess properties with these (12,6) parameters are comparable to those in Table 16 obtained with CH_4 as the reference fluid and (12,6) parameters of Sherwood and Prausnitz using the predicted values of f and g.

In order to determine the experimental Boyle properties of the $CH_4 + CF_4$ system, Douslin et al.[25] originally fit (n,6) potentials to the pure and cross-term second virial coefficients of CH_4, CF_4 and $CH_4 + CF_4$. The experimental Boyle properties were then determined from these potentials and has been done in the present work with the gas phase potentials in Table 14. Douslin and coworkers chose to represent the CH_4, CF_4 and $CH_4 + CF_4$ interactions by the (28,6), (500,6) and (30,6) potentials, respectively. These gas phase potentials have also been used to estimate parameters independent of the reference system for the various interactions with the (12,6) and (30,6)

Table 19. Potential parameters and excess properties independent of reference fluid.

| Molecular Pair | From Gas Phase Potentials Table 14 | | | | From Douslin's Gas Phase Potentials | | | |
| | (12,6) Potential | | (30,6) Potential | | (12,6) Potential | | (30,6) Potential | |
	ε/k (°K)	σ (Å)	ε/k (°K)	σ (Å)	ε/k (°K)	σ (Å)	ε/k (°K)	σ (Å)
$CH_4 + CH_4$	149.70	3.759	256.57	3.494	149.10	3.759	255.37	3.494
$CF_4 + CF_4$	151.60	4.682	259.82	4.352	151.66	4.669	259.92	4.340
$CH_4 + CF_4$	138.12	4.249	236.72	3.950	136.65	4.253	234.20	3.954

Predicted Excess Properties. (V^E in cm^3/mole; G^E in J/mole)

(2nd Order Calculation)	V^E	G^E	V^E	G^E	V^E	G^E	V^E	G^E
	0.63	231	0.26	384	1.03	252	0.48	418

potentials as was done with the gas phase potentials in Table 14. The parameters and corresponding excess properties are also given in Table 19. Results are comparable to those in Table 16 with experimental f and g. It can be seen that when values are available for gas phase potential parameters Eqs. (56) and (57) can be used to estimate parameters for any (n,6) potential to be used for the liquid phase, eliminating the need for some other source of liquid parameters and the arbitrary choice of reference fluids.

It should be mentioned that the total geometric mean rule of Chapter 2 can be applied to Douslin's like-pair gas phase potentials with good results. The unlike-pair potential parameters estimated in this way predict the cross-term second virial coefficient for the $CH_4 + CF_4$ pair with a root-mean-square deviation of 2.22 cm^3/mole.

Averaged Excess Properties

In the above scheme for estimating potential parameters independent of the reference system one choice still remains. One must choose the single (n,6) potential to be used in the one-fluid theory to represent all interactions in the liquid. For the $CH_4 + CF_4$ mixture the predicted excess properties are probably more sensitive to this choice than to either of the two choices eliminated by the above scheme. For mixtures of molecules which obey the same (n,6) potential in the liquid this potential would be the natural choice for the one-fluid potential. In the case of $CH_4 + CF_4$ system the choice is complicated by the fact that the two pure liquids require significantly different (n,6) potentials in perturbation theory as shown in Chapter 5.

One crude method for taking into account the different pair potentials obeyed by the different molecules is suggested by what has been done in the past with corresponding states mixture theories which employ pure fluid experimental data. With such theories it has been common practice with binary mixtures of molecules which are very different to calculate two sets of excess properties, one set with one liquid as reference and the second set with the other liquid as reference. The resulting two sets of excess properties can then be mole-fraction averaged to yield one set of values. Such a method may be used for vdW perturbation theory calculations by performing the calculations separately with both liquid potentials (parameters may be independent of the reference fluid) and mole-fraction averaging the resulting excess properties. Reasonably good choices for the liquid potentials for CH_4 and CF_4 would be the (12,6) and (30,6) potentials, respectively. These average excess properties for the equimolar mixture of $CH_4 + CF_4$ were computed from values in Table 19 and are shown in Table 20. From Table 20 it can be seen that even this crude method of taking into account the presence of molecules with different pair potentials gives better estimates of the experimental values than those predicted by either separate pair potential.

The dependence of predicted excess properties on the single pair potential chosen points out the necessity of somehow accounting for the different pair potentials obeyed by different molecules even when experimentally derived estimates are available for f and g of like-pair and unlike-pair interactions.

Table 20. Averaged excess properties[a] (parameters
independent of reference fluid).

	V^E (cm^3/mole)	G^E (J/mole)
Experimental data	0.845	360
Douslin's gas phase potentials (Exptl. f and g)	0.76	335
Gas phase potentials from Table 14 (Pred. f and g)	0.45	308

[a]Second order perturbation theory used with macroscopic compressibility
approximation to the second order term given in reference 29.

Conclusions

The one-fluid van der Waals prescription for mixture potential energy parameters in the perturbation theory of Barker and Henderson reproduces well the Monte Carlo calculations for the (12,6) potential.

The vdW perturbation model predicts the excess properties of the equimolar CH_4 + CF_4 liquid mixture when CH_4 is taken as the reference fluid with the (12,6) potential as well as the Leland, Rowlinson and Sather theory and better than the Leonard, Barker and Henderson theory using the like-pair and unlike-pair potential energy parameters in the ratios obtained from the experimental Boyle properties. Such predictions are shown to be dependent on a number of arbitrary choices, such as (1) the reference fluid, (2) the particular single pair potential for all interactions in the liquid, and (3) the source of potential parameters.

In view of the large variations in magnitudes of mixture and pure fluid properties predicted by the various potential energy functions and reference fluids it appears unlikely that it will be possible to predict the magnitude of both pure fluid and mixture properties with a single pair potential.

Probably the most important result of this work is the demonstration that most of the deviation of the unlike-pair energy parameter ϵ_{ij} from the geometric mean rule for the CH_4 + CF_4 system arises from forcing all pair interactions to obey one form of the pair potential.

It is further shown that knowledge of the single-component gas phase potentials with the mixture rules proposed in Chapter 2 allows the prediction of both like-pair and unlike-pair parameters for any

pair potential chosen to represent all interactions in the liquid. These parameters are independent of the choice of reference fluid, but they will depend on the particular liquid potential used. The same procedure for estimating liquid potential parameters is recommended when both like-pair and unlike-pair gas phase parameters are known as in the case of the $CH_4 + CF_4$ mixture.

Finally, a crude method is illustrated for taking into account the different pair potentials of the constituent molecules in the liquid mixture. The method predicts extremely good estimates of the excess properties of the equimolar $CH_4 + CF_4$ mixture.

CHAPTER 7

CORRESPONDING STATES FOR FLUID MIXTURES--NEW PRESCRIPTIONS

Introduction

The most accurate theories of fluid mixtures proposed to date
are the one-fluid and two-fluid van der Waals theories[21,22,30] and the
Leonard, Henderson, Barker multicomponent perturbation theory.[23] Limited
results for the one-fluid van der Waals theory and the multicomponent
perturbation theory were presented in Chapter 6 (Table 13) and compared
with Monte Carlo results. Extensive comparison of the one-fluid and
two-fluid van der Waals theories with Monte Carlo calculations for
both hard-sphere and (12,6) mixtures has been made by Henderson and
Leonard in references 30 and 31. Results show that the one-fluid
van der Waals theory is superior to the two-fluid van der Waals theory
and the three-fluid theory. In the previous chapter it was shown
(Table 16) that the one-fluid van der Waals (vdW) theory was superior
to the multicomponent perturbation theory for the methane + perfluoro-
methane system.

The one-fluid and two-fluid theories are corresponding states
models in which the thermodynamic properties of a mixture are related
to the properties of one or more imaginary fluids, respectively. The
van der Waals prescription is merely a prescription for calculating
composition-dependent potential energy parameters for the imaginary
fluids. Leland, Rowlinson and Sather[21] have examined the thermodynamic
consequences of the one-fluid van der Waals prescription for mixtures
of soft spheres and find it superior to other one-fluid theories.

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In the present chapter new prescriptions are presented for calculating potential parameters for the one or two imaginary fluids in either the one-fluid or the two-fluid theory. The prescriptions arise from exact statistical mechanical expressions for gas mixtures. The new prescriptions will be referred to as the virial coefficient (vc) prescriptions. The first to be discussed is called the Boyle prescription (vcB); it reduces to the van der Waals prescription for fluids which obey the van der Waals equation of state. The second is called the least squares prescription (vcls) and is the most general of the vc prescriptions.

The Boyle Prescription (vcB)

Statistical mechanics provides the following expression for the second virial coefficient $B_m(T)$ of a binary gas mixture.

$$B_m(T) = x_1^2 B_1(T) + 2x_1 x_2 B_{12}(T) + x_2^2 B_2(T) \quad . \tag{58}$$

The Boyle temperature of the mixture (T_{B_m}) is defined analogously to that of a pure component.

$$B_m(T_{B_m}) = 0 = x_1^2 B_1(T_{B_m}) + 2x_1 x_2 B_{12}(T_{B_m}) + x_2^2 B_2(T_{B_m}) \quad . \tag{59}$$

The Boyle volume of the mixture is given by

$$V_{B_m} = T_{B_m}(\partial B_m/\partial T)_{T_{B_m}} = T_{B_m}\{x_1^2(\partial B_1/\partial T)_{T_{B_m}} + 2x_1 x_2(\partial B_{12}/\partial T)_{T_{B_m}}$$

$$+ x_2^2(\partial B_2/\partial T)_{T_{B_m}} \} \quad . \tag{60}$$

Under the usual one-fluid assumption that the mixture at a given composition obeys two parameter corresponding states with some reference fluid, we have the following relations for the potential parameters ε_m and σ_m of the one fluid which will represent the mixture in terms of those of some reference fluid (R).

$$\varepsilon_m/\varepsilon_R = T_{B_m}/T_{B_R} \tag{61}$$

$$\sigma_m/\sigma_R = (V_{B_m}/V_{B_R})^{1/3} \; . \tag{62}$$

For any (n,6) potential T_{B_m} and V_{B_m} as well as T_{B_R} and V_{B_R} are readily evaluated using the series expansion for B(T) mentioned in Appendix A and its temperature derivative. In fact, for any (n,6) potential chosen to represent the one-fluid mixture it is unnecessary to consider a particular reference fluid. One can simply use the following relations.

$$(\varepsilon/k)_{m(n,6)} = T_{B_m}/T^*_{B_{(n,6)}} \; , \tag{63}$$

and

$$\sigma_{m(n,6)} = (V_{B_m}/V^*_{B_{(n,6)}})^{1/3} \; , \tag{64}$$

where

$$T^*_{B_{(n,6)}} = T_{B_{(n,6)}}/(\varepsilon/k)_{(n,6)} \; , \tag{65}$$

and

$$V^*_{B_{(n,6)}} = V_{B_{(n,6)}}/(N\sigma^3)_{(n,6)} \; . \tag{66}$$

Thus, the one-fluid Boyle (vcB) prescription is contained in either Eqs. (61) and (62) or Eqs. (63) and (64). The prescription yields

potential parameters for some fluid which, according to the corresponding states assumption, will have the same thermodynamic properties as the mixture of given composition at all temperatures and pressures. Unlike the parameters from the vdW prescription the parameters from the vcB prescription are exact within the corresponding states assumption.

The two-fluid vcB prescription is readily derived by writing Eq. (58) as

$$B_m(T) = x_1[x_1 B_1(T) + x_2 B_{12}(T)] + x_2[x_2 B_2(T) + x_1 B_{12}(T)] \quad ,$$

$$\tag{67}$$

or

$$B_m(T) = x_1 B_1'(T) + x_2 B_2'(T) \quad . \tag{68}$$

Here the mixture virial coefficient is given as that of an ideal mixture of two imaginary fluids with virial coefficients $B_1'(T)$ and $B_2'(T)$. The Boyle properties of the two fluids determine the potential parameters of these fluids to be used in two-fluid theory calculations.

Relation of the vcB Prescription to the vdW Prescription

For a single component van der Waals gas[32] the second virial coefficient is given by

$$B(T) = b - a/RT \quad , \tag{69}$$

where a and b are the usual van der Waals constants.

The Boyle temperature is given by

$$T_B = a/Rb \quad , \tag{70}$$

and the Boyle volume is given by

$$V_B = b \quad . \tag{71}$$

For a one-fluid mixture of van der Waals gases

$$T_{B_m} = a_m/Rb_m \quad , \tag{72}$$

and

$$V_{B_m} = b_m \quad . \tag{73}$$

Writing Eq. (59) for a van der Waals fluid,

$$0 = x_1^2(b_1 - a_1/RT_{B_m}) + 2x_1x_2(b_{12} - a_{12}/RT_{B_m}) + x_2^2(b_2 - a_2/RT_{B_m}) \quad . \tag{74}$$

Rearranging we have

$$T_{B_m} = (x_1^2 a_1/R + 2x_1x_2 a_{12}/R + x_2^2 a_2/R)/(x_1^2 b_1 + 2x_1x_2 b_{12} + x_2^2 b_2) \quad . \tag{75}$$

Using Eqs. (70) and (71) we obtain

$$T_{B_m} = (x_1^2 T_{B_1} V_{B_1} + 2x_1x_2 T_{B_{12}} V_{B_{12}} + x_2^2 T_{B_2} V_{B_2})/(x_1^2 V_{B_1} + 2x_1x_2 V_{B_{12}} + x_2^2 V_{B_2}) \quad . \tag{76}$$

$$V_{B_m} = T_{B_m}(x_1^2 a_1/RT_{B_m}^2 + 2x_1x_2 a_{12}/RT_{B_m}^2 + x_2^2 a_2/RT_{B_m}^2) \quad . \tag{77}$$

From Eqs. (76) and (77) we have

$$V_{B_m} = (x_1^2 V_{B_1} + 2x_1x_2 V_{B_{12}} + x_2^2 V_{B_2}) \quad . \tag{78}$$

Eqs. (76) and (78), when written in terms of ϵ/k and σ, are immediately

recognized as the van der Waals mixture rules given in Eqs. (51) and

(52) of Chapter 6.

Thus it is seen that the vcB and vdW prescriptions are identical for a van der Waals fluid, and the vcB prescription is for real systems the analog of the vdW prescription for van der Waals systems.

The vcB Prescription for (12,6) Systems

It should be pointed out that when evaluating the one-fluid or two-fluid vdW theories one is testing a combination of the one-fluid or two-fluid corresponding states assumption and the particular van der Waals prescription, since the van der Waals prescription would not be exact even if the corresponding states assumption were correct. With the vcB prescription, however, one is testing independently the corresponding states assumption since the vcB prescription is exact within the assumption of corresponding states. The most commonly used model for the intermolecular pair potential in real systems is the Lennard-Jones (12,6) potential. The properties of dilute Lennard-Jones gases in both pure and mixed states can be calculated from the series expansion for the (12,6) second virial coefficient. For pure and mixed dense liquid properties Monte Carlo computer simulation results are available for zero pressure. Monte Carlo calculations of McDonald at 115.8°K for potential parameters characteristic of the argon + krypton mixture have been reported by Leonard, Henderson and Barker.[23] Singer and Singer[33] have made similar calculations for other mixtures at 97°K. In the present work the Monte Carlo interpolation formulae of Singer and Singer[33] have been used to calculate the properties of pure (12,6) fluids as well as one-fluid and two-fluid mixtures using the vcB and vdW prescriptions. The resulting excess properties are compared to

the Monte Carlo estimates of both McDonald (Table 21) and Singer and
Singer (Tables 22-24).

As has already been shown[30,31] for the vdW prescription, the
one-fluid vcB prescription is superior to the two-fluid vcB prescription.
As a general rule the excess properties predicted by the one-fluid vcB
prescription are either equal to or slightly more negative than those
predicted by the vdW prescription. In almost every case, however, there
is little difference between the vcB and vdW results. Both one-fluid
prescriptions agree remarkably well with the Monte Carlo calculation.

Another comparison of the vcB and vdW prescriptions can be
made for gas phase mixtures using the second virial coefficient.
For a given set of like-pair and unlike-pair (12,6) parameters the
virial coefficient of an equimolar mixture can be calculated as a
function of temperature. Then the one-fluid vcB and vdW prescription
can be used to estimate the mixture virial coefficient. Results for
two sets of parameters are given in Table 25. The vcB prescription
is in these two cases seen to be superior to the vdW prescription,
but again it is seen that the difference between the two prescriptions
is not great.

The vcB Prescription for Mixtures of Molecules
with Different (n,6) Potentials

One of the most serious limitations of the one-fluid vdW theory
or one-fluid vcB theory as outlined above is the requirement that all
molecules and the mixture itself obey the same two-parameter
corresponding states or two-parameter pair potential. It was demonstrated
in Chapter 6 using the one-fluid vdW prescription that in order to make

Table 21. Comparison of one-fluid and two-fluid
prescriptions with Monte Carlo calculations.

T = 115.8°K, P = 0 and x_1 = x_2 = 0.5, ϵ_1/k = 119.8°K,

ϵ_2/k = 167.0°K, σ_1 = 3.405 Å, σ_2 = 3.633 Å, ϵ_{12} = $(\epsilon_1\epsilon_2)^{1/2}$,

σ_{12} = $(\sigma_1 + \sigma_2)/2$

Theory	G^E (J/mole)	H^E (J/mole)	V^E (cm^3/mole)
Monte Carlo[a]	34 ± 10	−34 ± 40	−0.54 ± .20
vcB[b]			
one-fluid	29	−34	−0.50
two-fluid	51	20	−0.32
vdW[c]			
one-fluid	42	−13	−0.46
two-fluid	57	30	−0.30
Multicomp. Pert.[d]	33	−49	−0.73

[a]McDonald's Monte Carlo calculations reported by Leonard et al.[23]

[b]Calculated from vcB prescription using Singer's[33] Monte Carlo inter-
polation formulae for properties of (12,6) fluids at P = 0.

[c]Calculated from vdW prescription using Singer's[33] interpolation
formulae.

[d]Taken from reference 23 for multicomponent perturbation theory.

Table 22. Comparison of excess free energy (G^E) from
vcB and vdW prescriptions with Monte Carlo
(MC) calculations.[a]

$$T = 97°K, \quad P = 0 \text{ and } x_1 = x_2 = .5, \quad \varepsilon_{12} = (\varepsilon_1 \varepsilon_2)^{1/2} = 133.5°K,$$

$$\sigma_{12} = (\sigma_1 + \sigma_2)/2 = 3.596. \quad G^E \text{ is in J/mole.}$$

σ_{11}/σ_{12}	1.00	1.03	1.08	1.12
$\varepsilon_{11}/\varepsilon_{12} = .810$				
G^E (MC)	130 ± 14	184 ± 14	(273)	(345)
G^E (vcB)				
one-fluid	123	188	280	342
two-fluid	118	149	205	225
G^E (vdW)				
one-fluid	145	209	301	362
two-fluid	129	160	107	236
$\varepsilon_{11}/\varepsilon_{12} = .900$				
G^E (MC)	35 ± 7	60 ± 7	97 ± 8	122 ± 10
G^E (vcB)				
one-fluid	31	61	100	121
two-fluid	30	44	62	71
G^E (vdW)				
one-fluid	37	66	105	127
two-fluid	32	47	65	74
$\varepsilon_{11}/\varepsilon_{12} = 1.000$				
G^E (MC)	1 ± 1	-2 ± 2	-12 ± 2	-21 ± 2
G^E (vcB)				
one-fluid	0	-2	-15	-35
two-fluid	0	-1	-10	-22
G^E (vdW)				
one-fluid	0	-2	-15	-35
two-fluid	0	-1	-10	-22

Table 22 (Continued)

σ_{11}/σ_{12}	1.00	1.03	1.08	1.12
$\varepsilon_{11}/\varepsilon_{12} = 1.111$				
G^E (MC)	35 ± 7	3 ± 7	-50 ± 10	-95 ± 10
G^E (vcB)				
one-fluid	31	-3	-69	-130
two-fluid	29	12	-23	-56
G^E (vdW)				
one-fluid	37	3	-64	-125
two-fluid	32	15	-20	-53

[a]MC calculations of J. V. L. Singer and K. Singer.[33] Values in
parentheses were estimated in reference 33 where no MC calculations
were available. Properties of all (12,6) fluids for evaluation
of vcB and vdW prescriptions were estimated using the MC interpolation
formulae in reference 33.

Table 23. Comparison of excess enthalpy (H^E) from
vcB and vdW prescriptions with Monte Carlo
(MC) calculations.[a]

$T = 97°K$, $P = 0$ and $x_1 = x_2 = 0.5$, $\varepsilon_{12} = (\varepsilon_1\varepsilon_2)^{1/2} = 133.5°K$,

$\sigma_{12} = (\sigma_1 + \sigma_2)/2 = 3.596$. H^E is in J/mole.

σ_{11}/σ_{12}	1.00	1.03	1.08	1.12
$\varepsilon_{11}/\varepsilon_{12} = .810$				
H^E (MC)	124 ± 34	(163)	(336)	(500)
H^E (vcB)				
one-fluid	78	174	330	453
two-fluid	95	142	238	286
H^E (vdW)				
one-fluid	111	206	362	484
two-fluid	111	159	111	301
$\varepsilon_{11}/\varepsilon_{12} = .900$				
H^E (MC)	29 ± 20	60 ± 7	167 ± 27	263 ± 35
H^E (vcB)				
one-fluid	20	67	145	206
two-fluid	24	47	87	118
H^E (vdW)				
one-fluid	28	75	153	214
two-fluid	28	51	91	122
$\varepsilon_{11}/\varepsilon_{12} = 1.000$				
H^E (MC)	1 ± 10	5 ± 12	54 ± 20	101 ± 24
H^E (vcB)				
one-fluid	0	0	0	0
two-fluid	0	0	0	0
H^E (vdW)				
one-fluid	0	0	0	0
two-fluid	0	0	0	0

Table 23 (Continued)

σ_{11}/σ_{12}	1.00	1.03	1.08	1.12
$\varepsilon_{11}/\varepsilon_{12}$ = 1.111				
H^E (MC)	34 ± 20	-12 ± 20	-48 ± 27	-40 ± 35
H^E (vcB)				
one-fluid	20	-28	-106	-167
two-fluid	23	0	-39	-70
H^E (vdW)				
one-fluid	28	-20	-98	-159
two-fluid	28	4	-35	-66

[a]MC calculations of J. V. L. Singer and K. Singer.[33] Values in
parentheses were estimated in reference 33 where no MC calculations
were available. Properties of all (12,6) fluids for evaluation of
vcB and vdW prescriptions were estimated using the MC interpolation
formulae in reference 33.

Table 24. Comparison of excess volume (V^E) from vcB
and vdW prescriptions with Monte Carlo (MC)
calculations.[a]

$T = 97°K$, $P = 0$ and $x_1 = x_2 = 0.5$, $\varepsilon_{12} = (\varepsilon_1 \varepsilon_2)^{1/2} = 133.5°K$,
$\sigma_{12} = (\sigma_1 + \sigma_2)/2 = 3.596$. V^E is in $cm^3/mole$.

σ_{11}/σ_{12}	1.00	1.03	1.08	1.12
$\varepsilon_{11}/\varepsilon_{12} = 0.810$				
V^E (MC)	-0.61 ± 0.19	-0.87 ± 0.19	(-1.29)	(-1.61)
V^E (vcB)				
one-fluid	-0.76	-0.94	-1.46	-2.05
two-fluid	-0.52	-0.71	-1.21	-1.80
V^E (vdW)				
one-fluid	-0.70	-0.89	-1.40	-1.99
two-fluid	-0.49	-0.68	-1.18	-1.77
$\varepsilon_{11}/\varepsilon_{12} = 0.900$				
V^E (MC)	-0.15 ± 0.09	-0.25 ± 0.09	-0.43 ± 0.11	-0.59 ± 0.17
V^E (vcB)				
one-fluid	-0.19	-0.30	-0.68	-1.18
two-fluid	-0.13	-0.24	-0.62	-1.11
V^E (vdW)				
one-fluid	-0.17	-0.28	-0.67	-1.16
two-fluid	-0.12	-0.23	-0.62	-1.11
$\varepsilon_{11}/\varepsilon_{12} = 1.000$				
V^E (MC)	0 ± 0.05	-0.01 ± 0.05	-0.02 ± 0.06	-0.02 ± 0.12
V^E (vcB)				
one-fluid	0	-0.05	-0.32	-0.72
two-fluid	0	-0.05	-0.32	-0.72
V^E (vdW)				
one-fluid	0	-0.05	-0.32	-0.72
two-fluid	0	-0.05	-0.32	-0.72

Table 24 (Continued)

σ_{11}/σ_{12}	1.00	1.03	1.08	1.12
$\varepsilon_{11}/\varepsilon_{12} = 1.111$				
V^E (MC)	-0.13 ± 0.09	-0.09 ± 0.09	0.00 ± 0.11	0.09 ± 0.17
V^E (vcB)				
one-fluid	-0.19	-0.17	-0.33	-0.65
two-fluid	-0.13	-0.11	-0.28	-0.59
V^E (vdW)				
one-fluid	-0.18	-0.15	-0.32	-0.64
two-fluid	-0.12	-0.10	-0.27	-0.59

[a]MC calculations of J. V. L. Singer and K. Singer.[33] Values in parentheses were estimated in reference 33 where no MC calculations were available. Properties of all (12,6) fluids for evaluation of vcB and vdW prescriptions were estimated using the MC interpolation formulae in reference 33.

Table 25. Comparison of the one-fluid vcB and vdW prescriptions for equimolar mixtures of (12,6) gases.

$$\varepsilon_1/k = 119.8°K, \quad \sigma_1 = 3.405 \text{ Å}, \quad \varepsilon_2/k = 167.00°K, \quad \sigma_2 = 3.633 \text{ Å},$$

$$\varepsilon_{12} = (\varepsilon_1\varepsilon_2)^{1/2}, \quad \sigma_{12} = (\sigma_1 + \sigma_2)/2$$

	Mixture Second Virial Coefficient (cm³/mole)			
T(°K)	Exact	vcB[a]	vdW[b]	Best fit (vcls)[c]
100.0	-264.47	-262.41	-261.61	-262.88
200.0	- 76.91	- 76.75	- 76.49	- 76.89
300.0	- 30.92	- 30.89	- 30.74	- 30.95
400.0	- 10.56	- 10.56	- 10.45	- 10.58
500.0	0.74	0.74	0.83	0.74
600.0	7.83	7.83	7.91	7.85
700.0	12.64	12.64	12.70	12.66
rms % dev		0.30	4.66	0.27

$$\varepsilon_1/\varepsilon_{12} = 1.111, \quad \sigma_1/\sigma_{12} = 1.08, \quad \varepsilon_{12} = (\varepsilon_1\varepsilon_2)^{1/2}, \quad \sigma_{12} = (\sigma_1 + \sigma_2)/2$$

$$\varepsilon_{12}/k = 133.5°K, \quad \sigma_{12} = 3.596 \text{ Å}$$

	Mixture Second Virial Coefficient (cm³/mole)			
T(°K)	Exact	vcB[d]	vdW[e]	Best fit (vcls)[f]
100.0	-255.51	-254.82	-254.49	-254.97
200.0	- 73.66	- 73.61	- 73.50	- 73.66
300.0	- 28.09	- 28.08	- 28.50	- 28.10
400.0	- 7.82	- 7.82	- 7.77	- 7.82
500.0	3.45	3.45	3.49	3.45
600.0	10.52	10.52	10.55	10.53
700.0	15.31	15.31	15.33	15.32
rms % dev		0.14	0.55	0.09

---

[a] $\varepsilon_m/k = 143.856°K \quad \sigma_m = 3.5205 \text{ Å}$

[b] $\varepsilon_m/k = 143.570°K \quad \sigma_m = 3.5210 \text{ Å}$

[c] $\varepsilon_m/k = 143.862°K \quad \sigma_m = 3.5225 \text{ Å}$, obtained from least squares fit of exact values.

[d] $\varepsilon_m/k = 135.659°K \quad \sigma_m = 3.6067 \text{ Å}$

Table 25 (Continued)

$^e \epsilon_m/k = 135.547°K \quad \sigma_m = 3.6075 \text{ Å}$

$^f \epsilon_m/k = 135.665°K \quad \sigma_m = 3.6080 \text{ Å}$, obtained from least squares fit of exact values.

accurate estimates of the excess properties of mixtures composed of molecules with very different (n,6) potentials some method must be used to account for the presence of different potentials. In this section two methods are examined which allow for the different potentials when the vcB prescription is used.

Mole-Fraction Averaged Excess Properties

The first of these methods is analogous to that used in Chapter 6. The method requires knowledge of liquid phase (n,6) potentials for pure components along with either gas phase or liquid phase unlike-pair potentials. To further illustrate the use of the vcB prescription only like-pair and unlike-pair Boyle temperatures and Boyle volumes are used. As in Chapter 6 the CH_4 + CF_4 mixture is used for demonstration purposes.

For the pure liquids CH_4 and CF_4 (n,6) potentials have been determined using second order perturbation theory as suggested in Chapter 5 by adjusting n so that predicted pure liquid densities equaled experimental densities at 111°K. The experimental densities were assumed to be at zero pressure. Parameters ε and σ for the (n,6) potentials were estimated using pure fluid Boyle properties calculated from Douslin's gas phase potentials for CH_4 and CF_4.[25] The macroscopic compressibility approximation to the second order term in perturbation theory is used. In this chapter the Carnahan-Starling hard-sphere equation of state and free energy has been used with Percus-Yevick hard-sphere radial distribution functions. Potentials found are given in Table 26 along with calculated molar volume and residual free energy.

Table 26. Liquid phase potentials for CH_4 and CF_4.

T = 111°K, P = 0, experimental densities taken from Table 18.

Liquid	n	ε/k(°K)	σ(Å)	V(cm^3/mole) Exptl	Calcd	Calculated G^r(J/mole)
CH_4	13.2	161.105	3.7172	37.70	37.70	-4226.2
CF_4	34.2	273.106	4.3141	49.47	49.47	-6688.3

Using both like-pair and unlike-pair gas phase potentials given by Douslin the Boyle temperature and Boyle volume of the $CH_4 + CF_4$ mixture are calculated at various compositions. Then all interactions in the liquid are assumed to obey the (13.2,6) potential found for liquid methane. Using the mixture Boyle properties one-fluid (13.2,6) potential parameters for the mixture at various compositions are estimated. With these parameters the molar volume and residual free energy of the mixture is calculated for each composition at zero pressure and 111°K. The (13.2,6) potential parameters of pure CF_4 are also estimated and used to calculate the pure liquid CF_4 properties at the same temperature and pressure. The excess properties are then calculated. In the same way excess properties are calculated assuming all interactions obey the (34.2,6) potential found for pure liquid CF_4. The resulting two sets of excess properties are then mole-fraction averaged to obtain one set of excess properties for the various mixture compositions. The two sets of excess properties for the two respective (n,6) potentials are given in Table 27. The mole-fraction averaged excess properties are given in Table 28. Results are also given in Figure 2 for excess free energy. The mole-fraction averaged excesses are the best estimates of the experimental values obtained to date with any theory which requires the use of a single pair potential for all intermolecular interactions.

Three-Parameter One-Fluid Theory

While it is possible to obtain good estimates of the excess properties of mixtures composed of molecules with different (n,6) potentials the preceding results again demonstrate that it is not

Table 27. Mixture properties and excess properties[a] for the CH_4 + CF_4 system with the (13.2,6) and (34.2,6) potentials. T = 111°K, P = 0, vcB prescription,[b] volumes in cm^3/mole, free energies in J/mole.

x_{CF_4}	(13.2,6) Potential				(34.2,6) Potential			
	V_m	G_m^r	V^E	G^E	V_m	G_m^r	V^E	G^E
.100	41.44	-4078.9	0.34	133.0	28.47	-6257.5	0.16	219.0
.245	46.74	-3965.1	0.71	241.5	32.05	-6083.9	0.34	399.6
.432	53.36	-3942.0	0.92	278.7	36.58	-6049.0	0.47	462.5
.500	55.70	-3960.0	0.98	270.7	38.19	-6076.3	0.48	449.9
.630	60.05	-4024.1	0.81	232.1	41.22	-6174.0	0.45	386.0
.835	66.65	-4188.0	0.54	121.4	45.86	-6422.9	0.27	203.0

Pure Fluid Properties

Liquid	(13.2,6) Potential		(34.2,6) Potential	
	V	G^r	V	G^r
CH_4	37.70	-4226.2	25.95	-6481.9
CF_4	71.73	-4362.0	49.47	-6688.3

---

[a]Excess properties calculated as discussed in Appendix C.

[b]Required Boyle properties calculated from Douslin's gas phase like-pair and unlike-pair potentials.[25]

Table 28. Averaged excess properties[a] from
vcB prescription.

$$T = 111°K, \ P = 0$$

x_{CF_4}	V^E (cm^3/mole)		G^E (J/mole)	
	Experimental[b]	Calculated	Experimental[b]	Calculated
.100	0.37	0.33	153.5	141.6
.245	0.71	0.62	297.7	280.2
.432	0.86	0.72	364.4	358.1
.500	0.845	0.73	359.9	360.3
.630	0.74	0.58	315.5	329.1
.835	0.39	0.31	167.7	189.5

---

[a]Mole-fraction averaged excess properties calculated as follows:

$$V^E_{AVG} = x_{CH_4} V^E_{(13.2,6)} + x_{CF_4} V^E_{(34.2,6)}$$

$$G^E_{AVG} = x_{CH_4} G^E_{(13.2,6)} + x_{CF_4} G^E_{(34.2,6)}$$

[b]Experimental excess properties at 111°K estimated from data of Croll
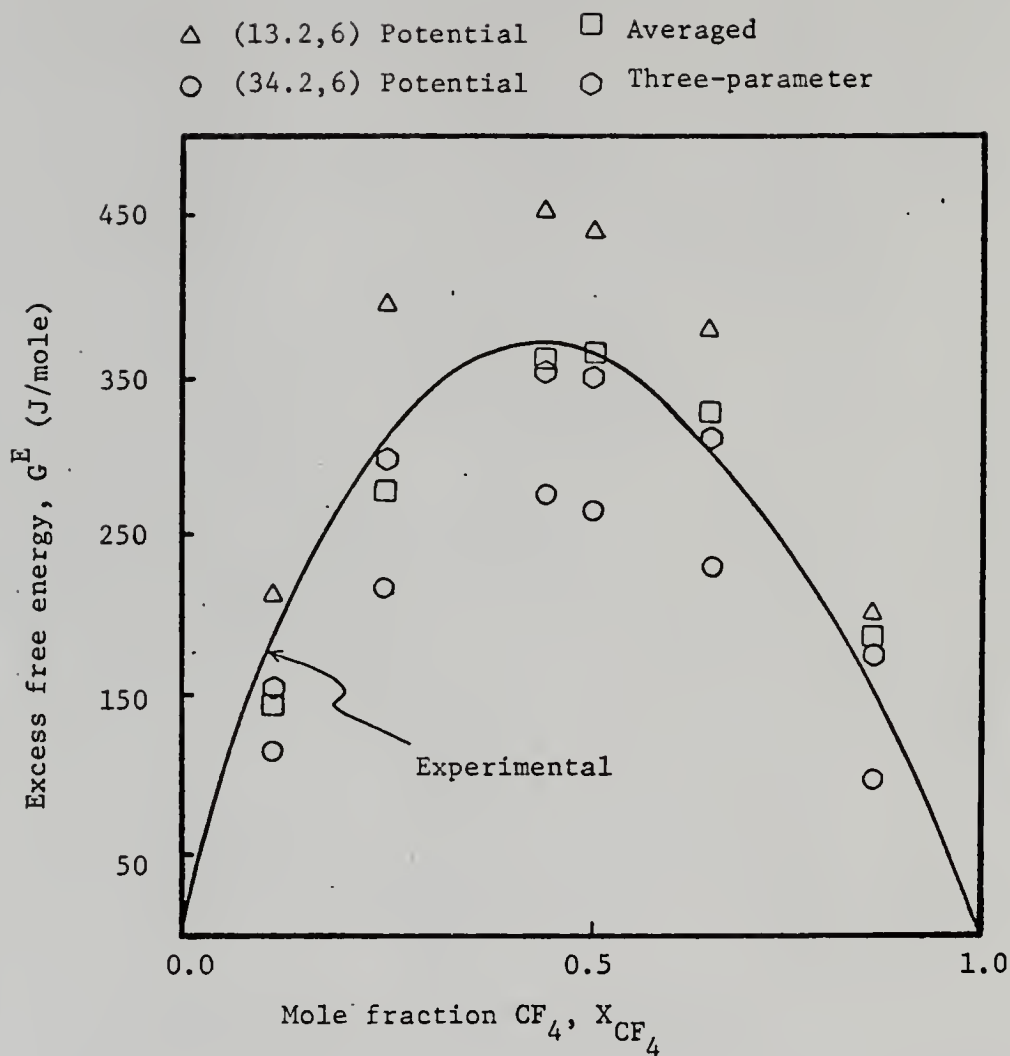and Scott as described in Appendix D.

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Figure 2. Excess free energy of the $CH_4 + CF_4$ system at 111°K, P = 0.

possible with the present one-fluid theory to predict the actual

mixture properties and both sets of pure fluid properties with a single

(n,6) potential. At present the only theory with sufficient flexibility

to allow the use of different pair potentials for different molecular

pairs is the multicomponent perturbation theory of which the Leonard,

Henderson, Barker theory[23] is one version. Unfortunately calculations

made with this theory are very expensive and of questionable accuracy

for such systems as the $CH_4 + CF_4$ system (Chapter 6, Table 16).

As mentioned before the one-fluid theory in its present form

does not have sufficient flexibility to allow the use of more than a

single pair potential for all interactions. The second method to be

discussed in this chapter for taking into account the different pair

potentials obeyed by different molecular pairs in a mixture is actually

an attempt to extend the one-fluid theory to three-parameter potentials.

This would give the one-fluid theory a flexibility equivalent to that

of multicomponent perturbation theory.

A binary mixture of species 1 and 2 at zero pressure and

fixed temperature is characterized by the following set of variables:

ϵ_1, σ_1, n_1, ϵ_2, σ_2, n_2, ϵ_{12}, σ_{12}, n_{12} and x_1. The three-parameter one-

fluid theory assumes that such a mixture can be represented by an

imaginary fluid with composition dependent potential parameters

ϵ_m, σ_m, n_m. It should be emphasized that Eq. (58) on which the Boyle

prescription is based does not require that the virial coefficients

B_1, B_{12} and B_2 obey the same pair potential. As a result the Boyle

properties calculated from Eqs. (59) and (60) are characteristic

of a mixture composed of intermolecular interactions represented by

B_1, B_{12} and B_2. If some means were available for estimating n_m as a function of n_1, n_2, n_{12} and composition, then the Boyle prescription could be used to estimate ε_m and σ_m. For the present investigation the following arbitrary relation has been assumed for n_m.

$$n_m = x_1^2 n_1 + 2x_1 x_2 n_{12} + x_2^2 n_2 \tag{79}$$

For mixtures in which all interactions obey the same (n,6) potential the three-parameter theory reduces to the two-parameter one-fluid vcB prescription. Values of n_{CH_4} and n_{CF_4} for the liquid are 13.2 and 34.2, respectively. Unfortunately, no accurate means of estimating n_{12} for the $CH_4 + CF_4$ pair in the liquid is available, and the resulting n_m and predicted liquid mixture properties are quite sensitive to the value of n_{12}. In order to determine n_{12} for use in Eq. (79) one piece of liquid experimental mixture data is required. The experimental molar volume of the equimolar liquid mixture at 111°K and zero pressure is used in this work. As was done for the pure fluids, a value of n_m was found to correctly predict the mixture volume. Values of ε_m and σ_m were estimated from the Boyle temperature and Boyle volume of the gas phase equimolar mixture according to the vcB prescription. The equimolar mixture was found to obey the (21.65,6) potential. Using Eq. (79) a value of 19.60 was found for n_{12}. This value was then used to calculate n_m at other compositions. For each composition T_{B_m} and V_{B_m} are calculated using Douslin's like-pair and unlike-pair gas phase potentials. These Boyle properties are used with the respective values of n_m to determine the corresponding values of ε_m and σ_m. The composition

dependent ε_m, σ_m and n_m are used to estimate the actual mixture proper-

ties as well as excess properties at 111°K and zero pressure. In this

case the ideal mixture properties are calculated using the (13.2,6)

and (34.2,6) potentials for liquid CH_4 and CF_4, respectively. Results

of the three-parameter one-fluid theory calculations are given in

Table 29. Results are also given in Figure 2 for excess free energy

and in Figure 3 for mixture volume. Both the predicted mixture proper-

ties and excess properties compare favorably with experimental properties.

This success suggests that the three-parameter one-fluid theory holds

promise for treating mixtures of molecules with different pair potentials.

The Virial Coefficient Least Squares (vcls) Prescription

Use of the vcB prescription forces the second virial coefficient

and its first temperature derivative at one temperature calculated

from the one-fluid theory to equal that of the mixture in question.

Since the corresponding states assumption on which the one-fluid theory

is based is only approximately correct, parameters calculated from the

vcB prescription do not give exactly correct mixture second virial

coefficients at all temperatures. While the vcB prescription gives

excellent results for both the mixture second virial coefficients and

liquid mixture excess properties, Eq. (58) can serve as the basis

for another one-fluid prescription. For a given mixture composition

Eq. (58) can be used to generate $B_m(T)$ over a range of temperature.

The resulting points may simply be fit by least squares to determine

the one-fluid potential parameters which represent the mixture behavior

at a given composition. Such a least squares fit is not expensive

and will result in the best possible set of one-fluid parameters at least

Table 29. Calculated mixture and excess properties
for the $CH_4 + CF_4$ system with the three-
parameter vcB prescription.

$$T = 111°K, \quad P = 0$$

| | Mixture Properties | | | Excess Properties | | | |
| | V_m(cm³/mole) | | Calculated | V^E(cm³/mole) | | G^E(J/mole) | |
x_{CF_4}	Exptl[a]	Calcd	G^r(J/mole)	Exptl[a]	Calcd	Exptl[a]	Calcd
.100	39.25	39.40	−4307.6	.37	.52	153.5	149.2
.245	41.29	41.46	−4515.7	.71	.88	297.7	287.4
.432	43.64	43.69	−4910.0	.86	.91	364.4	352.0
.500	44.43	44.43	−5082.1	.845	.845	359.9	348.9
.630	45.86	45.79	−5445.1	.74	.67	315.5	310.8
.835	47.92	47.83	−6100.8	.39	.30	167.7	171.0

Potential Parameters

x_{CF_4}	n_m	ε_m/k (°K)	σ_m (Å)
.100	14.56	170.03	3.786
.245	16.83	184.48	3.880
.432	20.26	204.92	3.994
.500	21.65	212.70	4.035
.630	24.52	227.97	4.110
.835	29.60	252.75	4.225

[a]Experimental properties at 111°K calculated as described in Appendix D.

△ (13.2,6) Potential   ○ Three-parameter

○ (34.2,6) Potential
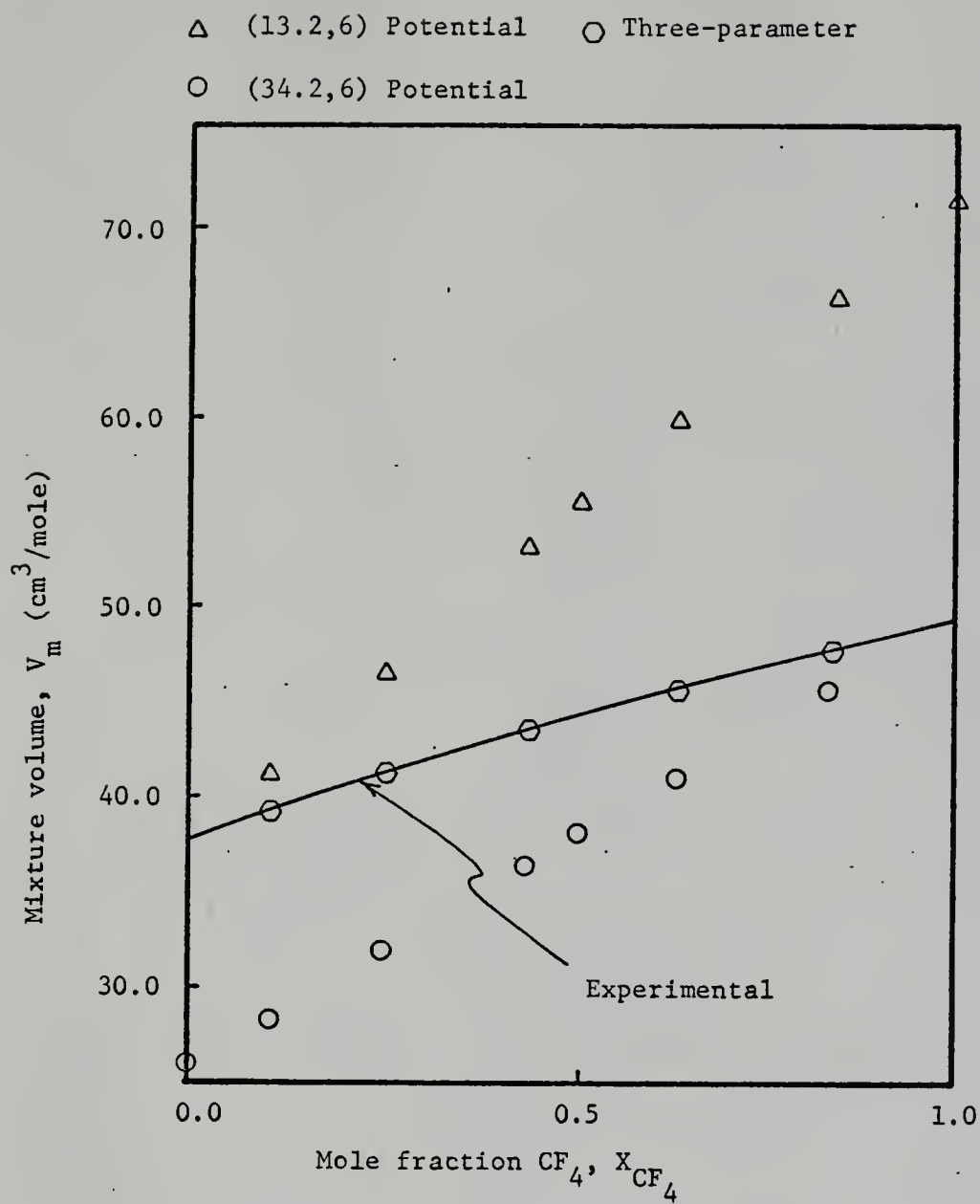
Figure 3.   Molar volume of the CH_4 + CF_4 system at 111°K, P = 0.

for the dilute gas mixtures. Calculations have been made for the properties of both gas phase and liquid phase mixtures of (12,6) molecules. These calculations were made for the two sets of potential parameters used in Table 25. The least squares program was written to minimize the sum of squares of the fractional deviations. The least squares (vcls) prescription, of course, gives the best reproduction of the gas phase mixture virial coefficients. These results are the best-fit values in Table 25. The liquid mixture excess properties are nearly the same as those predicted by the vcB prescription. Results are reported in Table 30.

Another calculation has been made for mixtures of (12,6) molecules. The second set of exact mixture virial coefficients in Table 25 has been used for a three-parameter least squares fit. This was done in order to determine the best ε_m, σ_m and n_m to represent the mixture of (12,6) molecules. If the one-fluid corresponding states assumption were completely correct one would expect the best n_m found for the mixture to be 12. The actual value of n_m found was 12.1, indicating that the mixture virial coefficients do nearly correspond to the (12,6) potential.

The vcls prescription holds little or no advantage over the vcB prescription for mixtures of molecules all of which obey the same two-parameter pair potential. The advantage of the vcls prescription may lie in its possible extension to a three-parameter one-fluid theory to treat mixtures of molecules which obey different pair potentials. Hanley and Klein[2] have pointed out the insensitivity of the second virial coefficient to the parameter n in the (n,6) potential over certain

Table 30. Comparison of the one-fluid vcls prescription[a] and Monte Carlo calculations.

$$\varepsilon_1/k = 119.8°K, \ \sigma_1 = 3.405 \ Å, \ \varepsilon_2/k = 167.00°K, \ \sigma_2 = 3.633 \ Å,$$

$$\varepsilon_{12} = (\varepsilon_1\varepsilon_2)^{1/2}, \ \sigma_{12} = (\sigma_1 + \sigma_2)/2, \ T = 115.8°K, \ P = 0$$

Theory	G^E (J/mole)	H^E (J/mole)	V^E (cm^3/mole)
Monte Carlo[b]	34 ± 10	−34 ± 40	−0.54 ± 0.20
vcls	27	−34	−0.44

$$\varepsilon_1/\varepsilon_{12} = 1.111, \ \sigma_1/\sigma_{12} = 1.08, \ \varepsilon_{12} = (\varepsilon_1\varepsilon_2)^{1/2}, \ \sigma_{12} = (\sigma_1 + \sigma_2)/2$$

$$\varepsilon_{12}/k = 133.5°K, \ \sigma_{12} = 3.596 \ Å, \ T = 97°K, \ P = 0$$

Theory	G^E (J/mole)	H^E (J/mole)	V^E (cm^3/mole)
Monte Carlo[c]	−50 ± 10	−48 ± 27	0.00 ± 0.11
vcls	−70	−106	−.32

[a] Properties of pure fluids and one-fluid mixtures calculated from the Monte Carlo interpolation formulae of Singer and Singer.[33]

[b] Monte Carlo results of McDonald reported in reference 23.

[c] Monte Carlo results of Singer and Singer reported in reference 33.

ranges of temperature. Assuming that the same is true for the mixture second virial coefficient the problem of lack of sensitivity could be avoided, since Eq. (58) can be used to generate exact values of $B_m(T)$ over any temperature range desired.

Conclusions

Two new prescriptions have been presented for use with either the one-fluid or two-fluid theory of mixtures. As was shown earlier for the vdW prescription the one-fluid vcB prescription appears to be somewhat superior to the two-fluid vcB prescription. Both the one-fluid vcB and vcls prescriptions yield accurate estimates of mixture second virial coefficients and liquid excess properties for mixtures of (12,6) molecules. The vcB prescription is shown to reduce to the vdW prescription for mixtures of molecules which obey the vdW equation of state. When used to calculate mole fraction averaged excess properties the vcB prescription yields accurate estimates of the excess properties of the $CH_4 + CF_4$ system at 111°K over the entire range of composition. A method is illustrated for extending the vcB prescription to provide a three-parameter one-fluid theory. Good estimates of both actual mixture properties and excess properties are possible.

Finally, it is proposed that the vcls prescription be extended to three parameters in order to treat mixtures of molecules which obey different pair potentials.

CHAPTER 8

ESTIMATION OF EXCESS PROPERTIES FOR VARIOUS SYSTEMS
USING THE TOTAL GEOMETRIC MEAN RULE IN THE GAS PHASE

Introduction

In the previous chapters methods have been developed for
(1) estimating gas phase unlike-pair potential energy parameters from
gas phase like-pair parameters (Chapter 2), (2) estimating like-pair
and unlike-pair liquid phase parameters from known gas phase parameters
(Chapter 6) and (3) estimating one-fluid mixture potential energy
parameters using the vcB and vcls prescriptions (Chapter 7). In the
present chapter these ideas are combined to estimate excess properties
of several binary liquid mixtures. No attempt is made to account for
the presence of molecules with different liquid phase (n,6) potentials.
Instead all calculations of pure liquid and mixed liquid properties
are made with the (12,6) potential using the Monte Carlo interpolation
formulae of Singer and Singer. As a result only excess properties of a
mixture are compared with experiment since pure component and mixture
properties may not be predicted accurately by the (12,6) potential.
The primary purpose of the present chapter is to further examine the
validity of the explanation offered in Chapter 6 for the deviation of
ε_{ij} from $(\varepsilon_i \varepsilon_j)^{1/2}$ usually observed in liquid mixture calculations.
Allowing for the different gas phase (n,6) potentials obeyed by CH_4
and CF_4 through use of the total geometric mean rule (Set A of Chapter
2) did account for most of the deviation of ε_{ij} from the geometric
mean observed in the liquid when all interactions were assumed to obey

the same (n,6) potential. The success of the total geometric mean

mixture rule for several binary gas phase mixtures in Chapter 2 suggests

that it may be possible for many mixtures to estimate both like-pair

and unlike-pair potential parameters to be used in the liquid phase.

Selection of Gas Phase (n,6) Potentials

Hanley and Klein[1,2] and Ahlert, Biguria and Gaston[3] have

studied the selection of (n,6) potentials from gas phase data.

Appendix A discusses the determination of the (n,6) potentials used

in Chapter 2. In general the (n,6) potential found to represent a

given molecule depends on the particular set of experimental gas data

used to determine the parameters. The potential found will depend

on the temperature range covered by the experimental data as well as

the accuracy of the data. As a result for a given molecule there is

often available a wide range of values of n found from fitting different

sets of data. The choice of the value of n to represent a molecule

is then somewhat arbitrary. Instead of making this choice for each

molecule in question another approach has been taken for the purpose

of demonstration. A value of n for CH_4 has been taken equal to 21 as

was done in Chapter 6. For other molecules the gas phase n is

adjusted so that the excess free energy of an equimolar liquid mixture

with CH_4 predicted by the one-fluid vcB theory agrees with the

experimental value. The total geometric mean rule is used for the

gas phase potentials, and the (12,6) potential is used for the liquid

phase. The parameters ε and σ for the (n,6) potentials used are

obtained by least squares from second virial coefficient data. For

mixtures not involving CH_4 the value of n for one molecule is held at that found from the mixture of that molecule with CH_4. The value of n for the other molecule is varied to obtain agreement between predicted and experimental excess free energy of the mixture in question. The procedure is analogous to the usual procedure of varying ξ discussed in Chapter 5 to obtain agreement with experimental excess free energy. The purpose is to demonstrate that the resulting values of n found for the gas phase from fitting the liquid mixture properties are reasonable values for the gas phase n. Since these values of n were obtained from the assumption of the total geometric mean rule in the gas phase, this supports the explanation proposed in Chapter 6 for the deviation of ε_{ij} in the liquid from the geometric mean.

The procedure followed is outlined below for the $Ar + CH_4$ mixture.

(1) CH_4 is assumed to obey the (21,6) potential in the gas phase.

(2) A gas phase value of n for Ar is assumed, and parameters ε and σ for this value of n are found by least squares from the second virial coefficient.

(3) Unlike gas phase parameters (n_{ij}, ε_{ij} and σ_{ij}) are calculated for the $Ar + CH_4$ pair using the total geometric mean rule of Chapter 2.

(4) Using Eqs. (56) and (57) from Chapter 6 like-pair and unlike-pair parameters are estimated for the (12,6) potential from the gas phase potentials.

(5) Using the vcB prescription of Chapter 7 one-fluid mixture

(12,6) parameters are calculated for the equimolar

mixture.

(6) With parameters from steps (4) and (5) the properties of

the pure fluids and the one-fluid mixture are calculated

at 91°K from the Monte Carlo interpolation formulae of

Singer and Singer.

(7) The excess properties are then calculated and the excess

free energy compared to the experimental value.

(8) If the calculated and experimental excess free energies

do not agree, a new value of n for argon is guessed, and

the procedure is repeated until the excess free energies

agree.

The resulting gas phase values of n for various molecules in binary

mixtures with CH_4 are given in Table 31 along with various values of

n for the same molecules found from gas phase second virial coefficient

data. The values of n found from fitting the liquid mixture data

appear to be reasonable values for use in the gas phase.

For mixtures which do not contain CH_4 the value of n for one

of the components is fixed at the value found for this component in

the presence of CH_4. The n for the other component is varied to obtain

agreement between calculated and experimental equimolar excess free

energy. The resulting values for n in these mixtures are given in Table

32. Again the values are reasonable values of n for the gas phase.

There are some inconsistencies in the results of Table 31 and Table 32.

For example the apparent value of n_{Ar} = 16.0 when in the presence of

$N_2(n_{N_2}$ = 16.0), while n_{Ar} = 11.25 in the presence of $CH_4(n_{CH_4}$ = 21.0).

Table 31. Gas phase values of n for various molecules found from liquid mixtures with CH_4.

Potential for CH_4 chosen as (21,6).

Gas Phase n

Molecule	This work[a]	From second virial coefficient
Ar	11.25	$9.0^{[b]}$–$20.0^{[c]}$
Kr	17.0	$18.0^{[b]}$
N_2	16.0	$19.31^{[c]}$
CO	17.0	$13.59^{[d]}$
CF_4	230.0	$136.3^{[c]}$–$\infty^{[e]}$

[a] Parameters ε/k and σ for these potentials given in Table 33.

[b] Value of n found by Klein in reference 1.

[c] Taken from Table 1.

[d] Value found from three parameter fit of data compiled by J. H. Dymond and E. B. Smith, The Virial Coefficients of Gases (Clarendon, Oxford, 1969).

[e] Value of n in the Sutherland potential used by Sherwood and Prausnitz.[12]

Table 32. Gas phase values of n for various molecules
found from liquid mixtures not containing CH_4.

Binary Mixture Component			
1	2	n_1 [a]	n_2 [b]
Ar	Kr	11.25	17.0
N_2	Ar	16.0	16.0
Ar	O_2	11.25	16.5
N_2	O_2	16.0	16.0
Ar	CO	11.25	13.5

---

[a] Value of n for component 1 is taken as the value in Table 31.

[b] Value of n for component 2 is found by varying it to obtain agreement
between calculated and experimental excess free energy for the
particular binary liquid mixture. Parameters for these potentials
are given in Table 33.

Similarly, $n_{CO} = 17.0$ in the presence of $CH_4(n_{CH_4} = 21.0)$, while

$n_{CO} = 13.5$ when in the presence of $Ar(n_{Ar} = 11.25)$. For other systems

which have components in common the results are consistent. This is

seen in that $n_{Kr} = 17.0$ when in the presence of both $CH_4(n_{CH_4} = 21.0)$

and $Ar(n_{Ar} = 11.25)$. Similarly, $n_{O_2} = 16.0$ when in the presence of

$N_2(n_{N_2} = 16.0)$, and n_{O_2} is nearly the same value when in the presence

of $Ar(n_{Ar} = 11.25)$. Parameters ε and σ for gas phase potentials used

in this chapter are given in Table 33. Some of the inconsistency may

be due to the approximate nature of the $(n,6)$ potential especially

for systems in which angular dependent forces are present. Part of

the inconsistency may be due to use of the $(12,6)$ potential for all

liquid interactions and to the particular choice of parameters ε and σ

for the potentials used in the gas phase. The latter two problems were

dealt with in Chapter 6. The remainder of the inconsistency can

probably be attributed to the approximate validity of the total geometric

mean rule.

The use of the total geometric mean rule in the gas phase will

always predict $\xi \leq 1.0$ for the liquid potential. The value of the

predicted ξ is equal to 1.0 only when the two molecules obey the same

$(n,6)$ potential in the gas phase. The values of ξ predicted by the

total geometric mean rule and the gas phase $(n,6)$ potentials are given

in Table 34 along with estimated like-pair and unlike-pair $(12,6)$

parameters for the various binary mixtures. Calculated and experimental

excess properties are given in Table 35. Two sets of $(12,6)$ parameters

and calculated excess properties are given for the $N_2 + Ar$ mixture.

Table 33. Gas phase potential parameters for various
molecules.

Molecule	(n,6) Potential	ϵ/k	σ	Source of parameters
CH_4	(21,6)	218.0	3.567	a
Ar	(11.25,6)	113.34	3.457	b
	(16,6)	147.93	3.329	b
Kr	(17,6)	217.36	3.526	c
	(18,6)	224.16	3.500	c
N_2	(16,6)	118.88	3.639	b
CO	(17,6)	129.27	3.634	b
	(13.5,6)	110.18	3.714	b
O_2	(16,6)	145.30	3.378	b
	(16.5,6)	148.23	3.369	b
CF_4	(136.3,6)	373.31	4.186	a
	(230,6)	395.32	4.159	b
C_2H_6	(17.74,6)	273.82	4.606	a

[a] Parameters from Table 1.

[b] Parameters from least squares fit of second virial coefficient data
compiled by J. H. Dymond and E. B. Smith, The Virial Coefficients of
Gases (Clarendon, Oxford, 1969).

[c] Parameters taken from reference 1.

Table 34. Like-pair and unlike-pair (12,6) potential parameters estimated from gas phase (n,6) potentials.

Binary Mixture[a]	Molecular Pair	(12,6) Parameters ε/k	σ
$CH_4 + Ar$	$CH_4 + CH_4$	149.70	3.759
(ξ = .9706)	$Ar + CH_4$	130.09	3.608
	$Ar + Ar$	120.00	3.429
$CH_4 + Kr$	$CH_4 + CH_4$	149.70	3.759
(ξ = .9974)	$CH_4 + Kr$	158.38	3.708
	$Kr + Kr$	168.44	3.654
$CH_4 + N_2$	$CH_4 + CH_4$	149.70	3.759
(ξ = .9955)	$CH_4 + N_2$	119.20	3.758
	$N_2 + N_2$	95.78	3.752
$CH_4 + CO$	$CH_4 + CH_4$	149.70	3.759
(ξ = .9974)	$CH_4 + CO$	122.14	3.765
	$CO + CO$	100.18	3.767
$CH_4 + CF_4$	$CH_4 + CH_4$	149.70	3.759
(ξ = .8869)	$CH_4 + CF_4$	133.63	4.262
	$CF_4 + CF_4$	151.64	4.673
$Ar + Kr$	$Ar + Ar$	120.00	3.429
(ξ = .9853)	$Ar + Kr$	140.08	3.548
	$Kr + Kr$	168.44	3.654
$N_2 + Ar$	$N_2 + N_2$	95.71	3.784
(ξ = 1.0000)	$N_2 + Ar$	107.17	3.602
	$Ar + Ar$	120.00	3.429
$N_2 + Ar$[b]	$N_2 + N_2$	100.15	3.620
(ξ = 1.0000)	$N_2 + Ar$	109.54	3.511
	$Ar + Ar$	119.80	3.405

Table 34 (Continued)

Binary Mixture[a]	Molecular Pair	(12,6) Parameters ϵ/k	σ
Ar + O_2	Ar + Ar	120.00	3.429
(ξ = .9871)	Ar + O_2	116.99	3.463
	O_2 + O_2	117.06	3.483
N_2 + O_2[b]	N_2 + N_2	100.15	3.620
(ξ = 1.0000)	N_2 + O_2	110.74	3.502
	O_2 + O_2	122.44	3.388
Ar + CO	Ar + Ar	120.00	3.429
(ξ = .9967)	Ar + CO	109.26	3.595
	CO + CO	100.15	3.765

[a]Values of ξ are calculated from predicted (12,6) parameters.

[b]These like-pair (12,6) parameters taken from reference 23. Unlike-pair parameters are the geometric mean of the like-pair parameters.

Table 35. Estimated excess properties using (12,6)
parameters from Table 34.

Binary Mixture	Excess Property	Calculated	Experimental[a]
CH_4 + Ar (91°K)	G^E	74	74
	H^E	93	103
	V^E	0.17	0.17
CH_4 + Kr (116°K)	G^E	31	30
	H^E	38	
	V^E	− 0.06	− 0.01[b]
CH_4 + N_2 (91°K)	G^E	139	135
	H^E	96	
	V^E	− 1.00	− 0.21
CH_4 + CO (91°K)	G^E	115	115
	H^E	80	105
	V^E	− 0.79	− 0.32
CH_4 + CF_4 (111°K)	G^E	360	360
	H^E	618	
	V^E	1.35	0.84[c]
Ar + Kr (116°K)	G^E	80	84
	H^E	46	
	V^E	− 0.32	− 0.53
N_2 + Ar[d] (84°K)	G^E	69	34
	H^E	85	51
	V^E	− 0.58	− 0.18
N_2 + Ar[e] (84°K)	G^E	40	34
	H^E	45	51
	V^E	− 0.27	− 0.18

Table 35 (Continued)

Binary Mixture	Excess Property	Calculated	Experimental[a]
Ar + O_2 (84°K)	G^E	38	37
	H^E	59	60
	V^E	0.16	0.14
N_2 + O_2 (78°K)	G^E	50	43
	H^E	56	46
	V^E	− 0.28	− 0.21
Ar + CO (84°K)	G^E	58	57
	H^E	78	
	V^E	− 0.37	+ 0.10

[a]Unless otherwise specified experimental data are the same as those used in reference 22.

[b]Taken from the review by R. Battino, Chem. Rev. 71, 5 (1971).

[c]Taken from Table 16.

[d]Excess properties calculated from first set of N_2 + Ar parameters in Table 34. These parameters were estimated from the gas phase potentials.

[e]Excess properties calculated from the second set of N_2 + Ar parameters in Table 34. These parameters are the (12,6) parameters used in reference 23.

Comparison of the two sets of excess properties demonstrates the sensitivity of the results to the source of parameters. Just as ε_{ij} estimated for the (12,6) potential will always be <u>less</u> <u>than</u> or equal to $(\varepsilon_i \varepsilon_j)^{1/2}$, σ_{ij} estimated for the (12,6) potential will always be <u>greater</u> <u>than</u> or equal to $(\sigma_i \sigma_j)^{1/2}$. When the gas phase potentials for a pair of molecules differ significantly as in the case of Ar + CH_4, the estimated σ_{ij} is even larger than $(\sigma_i + \sigma_j)/2$. When this is the case calculated excess volumes are more positive than those calculated from the assumption of $\sigma_{ij} = (\sigma_i + \sigma_j)/2$ in the liquid. This is the reason for the success of the method used for the mixtures Ar + CH_4 and Ar + O_2. The usual assumption of an arithmetic mean σ_{ij} does not predict sufficiently large excess volumes for these two mixtures. For some other mixtures, however, the arithmetic mean σ_{ij} would be an improvement over the σ_{ij} predicted from the gas phase potentials. The Ar + Kr mixture is one such case where a slight improvement would be seen if σ_{ij} were taken to be the arithmetic mean in the liquid.

Mention should be made of the rather large negative excess volumes observed for the mixtures Ar + CO, CH_4 + CO and CH_4 + N_2. In the latter two cases use of the arithmetic mean σ_{ij} in the liquid would result in even more negative values. In the first case there would be only a slight improvement if the arithmetic mean σ_{ij} were used in preference to the value predicted on the basis of the total geometric mean rule in the gas phase. As a result another explanation for the large negative value must be sought. Calculations were repeated using the one-fluid vdW prescription. Similar results were obtained indicating that the problem does not arise from use of the

vcB prescription. Therefore, it must be concluded that the large
negative values resulted from either the use of the particular set
potential parameters or the use of the (12,6) potential for all
interactions in the liquid.

Mixtures of Molecules with Very Different (n,6) Potentials

The systems discussed to this point except for the CH_4 + CF_4
system were all composed of molecules with similar (n,6) potentials
with n ranging from 11.25 to 21.0. In these systems ξ does not differ
significantly from the value 1.0. The systems for which a method for
estimating ξ is most desirable are those which contain molecules with
very different (n,6) potentials. It is for these systems that ξ
must be significantly less than 1.0. To demonstrate the usefulness
of the total geometric mean rule in the gas phase for estimating unlike-
pair liquid phase potential parameters in systems which exhibit large
deviations of ξ from 1.0, calculations are made for three such systems.
These systems are the CH_4 + CF_4 system treated earlier, the C_2H_6 + CF_4
system and the Kr + CF_4 system.

For these systems n for pure components is not found by fitting
the liquid mixture excess properties as was done in the previous
section. Instead, for each pure component n is selected somewhat
arbitrarily from values available from least squares fits of second
virial coefficient data. For CH_4 the (21,6) potential is used. For
CF_4 and C_2H_6 the (136.3,6) and (17.74,6) potentials, respectively, are
used. For Kr the (18,6) potential found by Klein[1] is used. The

parameters for these potentials are given in Table 33. Estimated like-pair and unlike-pair (12,6) parameters for the various interactions are given in Table 36. The calculated and experimental excess properties are given in Table 37. The results are quite good considering the fact that the (12,6) potential is not a good potential for some of the molecules involved and the fact that no experimental binary mixture data were used in the determination of unlike-pair parameters.

Conclusions

The total geometric mean rule for gas phase (n,6) potentials can be useful for estimating unlike-pair potential parameters for use in liquid mixture calculations. The method used is most applicable to systems containing molecules with very different (n,6) potentials.

Table 36. Like-pair and unlike-pair (12,6) potential
parameters estimated from gas phase (n,6)
potentials.

(Gas phase potentials were obtained from least squares fit of
second virial coefficients.)

Binary Mixture	Molecular Pair	(12,6) Parameters	
		ε/k	σ
$CH_4 + CF_4$ ·	$CH_4 + CH_4$	149.70	3.759
(ξ = .9169)	$CH_4 + CF_4$	138.13	4.249
	$CF_4 + CF_4$	151.60	4.682
$C_2H_6 + CF_4$	$C_2H_6 + C_2H_6$	206.73	4.791
(ξ = .8944)	$C_2H_6 + CF_4$	158.33	4.815
	$CF_4 + CF_4$	151.60	4.682
$Kr + CF_4$	$Kr + Kr$	167.77	3.645
(ξ = .8965)	$Kr + CF_4$	142.97	4.199
	$CF_4 + CF_4$	151.60	4.682

Table 37. Estimated excess properties using estimated
(12,6) parameters from Table 36.

Binary Mixture	Excess Property	Calculated	Experimental
$CH_4 + CF_4$ (116°K)	G^E	255	360
	H^E	449	
	V^E	0.59	0.845[a]
$C_2H_6 + CF_4$ (107°K)	G^E	550	632[b]
	H^E	731	
	V^E	2.52	
$Kr + CF_4$ (117°K)	G^E	424	314[b]
	H^E	721	
	V^E	0.42	

[a]Taken from Table 16.

[b]Taken from R. L. Scott, J. Phys. Chem. 62, 136 (1958).

CHAPTER 9

CONCLUSIONS

1. A geometric mean rule for each of the three parameters $(\varepsilon, \sigma$ and n) in the Mie (n,6) potential predicts accurate estimates of the cross-term second virial coefficients for many unlike-pairs of molecules. This set of geometric mean rules is called the total geometric mean rule.

2. The total geometric mean rule for the Mie (n,6) potential suggests that when molecules obey the same form of the pair potential the mixture rules for the energy and distance parameters should be the geometric mean. This is supported by the agreement between calculated and experimental cross-term second virial coefficients of unlike-pairs of molecules which obey the Dymond and Alder numerical potential.

3. The (n,6) and exponential-6 potentials are sufficiently alike with respect to the prediction of second virial coefficients that sets of three exponential-6 parameters can be used for the three parameters in the (n,6) potential. The total geometric mean rule for the (n,6) potential parameters can also be used for the exponential-6 potential parameters.

4. The best (n,6) potentials obtained by Hanley and Klein for second virial coefficients yield better estimates in perturbation theory of residual properties of liquids than those calculated with Hanley and Klein (12,6) potentials.

5. The (n,6) potentials found to give the best estimates of liquid properties in perturbation theory have values of n between the best value of n for the gas phase and the value 12.

6. In every case studied the best value of n found for use in the liquid phase is the largest value of n which predicts positive pressures for saturated liquid densities. This suggests that (n,6) potentials for liquids may be found by choosing n so that some experimental liquid density is correctly predicted by perturbation theory.

7. The use of the one-fluid van der Waals prescription for mixture potential energy parameters in perturbation theory reproduces Monte Carlo (12,6) calculations for excess properties of liquid mixtures as well as the multicomponent perturbation theory of Leonard, Henderson and Barker. The one-fluid van der Waals perturbation theory yields better estimates of the experimental excess properties of the $CH_4 + CF_4$ system than the multicomponent perturbation theory. The failure of the multicomponent perturbation theory for the $CH_4 + CF_4$ system is probably due to the treatment of the unlike-pair hard-sphere diameter in this theory.

8. Predictions of the one-fluid theory are dependent on the choice of (1) the reference fluid, (2) the single two-parameter pair potential for all interactions in the liquid, and (3) the source of potential parameters.

9. It is not possible to predict the correct magnitude of both pure liquid and liquid mixture properties with a single two-parameter pair potential when the pure components obey different (n,6) potentials in the liquid phase.

10. Most of the deviation of the unlike-pair energy parameter ϵ_{ij} from the geometric mean for the $CH_4 + CF_4$ pair which is usually observed in mixture calculations results from the artificial requirement that both molecules obey the same two-parameter pair potential. By

allowing different molecules to obey different two-parameter pair potentials in the gas phase ϵ_{ij} can be set equal to the geometric mean of the two like-pair parameters according to the total geometric mean rule.

11. Using the like-pair three-parameter gas phase potentials and the unlike-pair three-parameter gas phase potentials obtained from either the total geometric mean rule or some other source, parameters ϵ and σ can be estimated for both like-pair and unlike-pair interactions in any single two-parameter pair potential (e.g., the (12,6) potential) to be used for all interactions in either gas or liquid mixtures.

12. Using relations involving the like-pair and unlike-pair Boyle properties of molecules it is possible to estimate both like-pair and unlike-pair potential parameters which are independent of the choice of reference fluids.

13. It is possible with the one-fluid theory of mixtures to account for the presence of molecules with different pair potentials by mole-fraction averaging sets of excess properties predicted with each of the pure component pair potentials.

14. Statistical mechanics provides relations for calculating one-fluid or two-fluid mixture potential energy parameters. The two new virial coefficients prescriptions presented are shown to give accurate estimates of the properties for both gas and liquid mixtures of (12,6) molecules. The van der Waals prescription is a special case of one of the virial coefficient prescriptions.

15. Using the one-fluid virial coefficient Boyle prescription, mole-fraction averaged excess properties are accurate estimates of the

experimental excess properties for the $CH_4 + CF_4$ system at all compositions.

16. A three-parameter one-fluid virial coefficient prescription allows accurate estimation of both mixture properties and excess properties for systems of molecules with different (n,6) potentials.

17. The total geometric mean rule for gas phase (n,6) potentials is useful for estimating unlike-pair potential parameters for use in liquid mixture calculations. The method used is most applicable to systems containing molecules with very different gas phase (n,6) potentials and obviates the need for empirical determination of unlike-pair parameters.

APPENDICES

APPENDIX A

DETERMINATION OF (n,6) POTENTIALS FROM THE SECOND
VIRIAL COEFFICIENT

The values of ε, σ, and n for the pure systems studied were
determined from a least squares fit of the experimental second virial
coefficient using a least squares program based on the method of
M. J. D. Powell.[34] The common series expression[26] was used to repre-
sent the second virial coefficient for the Mie (n,6) potential.
Hanley[2] and Klein[1,2] have recommended that for determining potential
energy parameters emphasis be placed on the use of data in the
reduced temperature range below $T^*_{12,6} = 2.0$, where the reducing parameter
for the temperature is the value of ε/k for the Lennard-Jones (12,6)
potential. Unfortunately for many of the binary systems for which
data exist the experimental values for the pure components are not
available in this low reduced temperature range. Thus even though
the present investigation employed data over as wide a temperature range
as possible, more than one set of potential parameters ε, σ and n
exist for at least some of the pure systems which can be identified
with local minima in the sum-of-squares objective function. The
parameters are listed in Table 1 that reproduce the experimental second
virial coefficients for the single-component systems in the temperature
ranges and with the root-mean-square deviations shown. Where more
than one set of parameters was found, the set which gave the lowest
value for the best sum of squares of the deviations was used.

One further comment should be made. The root-mean-square
deviation for CF_4 (0.12 cm^3/mole) given in Table 1 is greater than the

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value of 0.05 cm^3/mole for CF_4 found by Sherwood and Prausnitz[12] with the best set of parameters for the Sutherland (∞,6) potential using the same smoothed second virial coefficient data. This suggests that the Mie (136.30,6) potential used in this work, while giving an excellent fit, is not the "best" Mie (n,6) potential for the CF_4 data. However, the value of n = 136.30 was retained on the basis of the value of 138.68 found for the repulsion exponent of SF_6, a similar molecule.

APPENDIX B

RESIDUAL THERMODYNAMIC PROPERTIES

Properties reported in Chapter 5 are residual properties.
These are defined by

$$X_{T,V}^r = X_{T,V}^{liquid} - X_{T,V}^{ideal\ gas} \qquad (B-1)$$

where X is any thermodynamic property. For internal energies the
residual properties are the same as configurational properties.
Rowlinson[35] gives values for the experimental configurational energy
argon, methane and nitrogen in the saturated liquid state. Entropies
for liquid argon were taken from reference 36. The ideal gas values
at the same T and V were calculated from the monatomic ideal gas
partition function and subtracted from values of entropy in reference
36 to obtain experimental residual entropies.

Din[37] gives entropies of liquid methane and nitrogen along the
saturation curve. Interpolation between state points was carried out
using the following equation

$$\Delta S = C_\sigma \ln(T_2/T_1) \qquad (B-2)$$

where C_σ is the heat capacity of a liquid which is maintained at all
temperatures in equilibrium with an infinitesimal amount of vapor.
This quantity is tabulated by Rowlinson.

.Din gives values of the entropy of methane in the ideal gas
state at one atmosphere. These were corrected for the effect of pressure
using the ideal gas partition function to yield entropies of the ideal

gas at saturated liquid temperatures and volumes. Ideal gas entropies
of nitrogen at saturated liquid conditions were calculated from the
partition function for an ideal diatomic gas and the physical constants
given on page 431 of reference 38. It should be pointed out that the
value given in this reference for the mass of a nitrogen molecule is in
error.

In the case of perfluoromethane ideal gas energies and entropies
at one atmosphere are tabulated in reference 39. Entropies were again
corrected for the effect of pressure using the ideal gas partition
function. The experimental saturated liquid energies and entropies
were taken from reference 40. The values reported for CF_4 are relative
to 116.49°K, taken arbitrarily as the zero for energy and entropy.
Calculated values reported for these properties for a given (n,6)
potential were obtained by subtracting predicted quantitites at
116.49°K from energies and entropies at other state points.

The program for evaluating the hard-sphere radial distribution
function and its density derivative was written by K. Rajagopal.[41]

APPENDIX C

CALCULATION OF EXCESS FREE ENERGY

Perturbation theory provides a means of calculating the residual properties of fluids. These properties are defined in Appendix B. For mixing at constant pressure and temperature the excess thermal properties of a mixture are not merely the differences between the residual properties of the mixture and the mole-fraction averages of the respective residual properties of the pure components. This is the result of the fact that all of the fluids (the mixture and the pure components) are not at the same volume when pressure and temperature are fixed. The following expression was used to calculate the excess Gibbs free energy (G^E) at zero pressure for a binary mixture from the residual free energy of the mixture (G_m^r) and that of the two pure components (G_1^r and G_2^r).

$$G^E = G_m^r - (x_1 G_1^r + x_2 G_2^r) + RT \ln(V_1^{x_1} V_2^{x_2}/V_m) \qquad \text{(C-1)}$$

All calculations of liquid properties in Chapter 6 have been made with the perturbation theory of Barker and Henderson.[14] Second order calculations employed the macroscopic compressibility approximation. Percus-Yevick hard-sphere radial distribution functions and free energies have been used. Carnahan-Starling[18] hard-sphere pressures and compressibilities have been used. Volumes for pure liquids and liquid mixtures at zero pressure were determined by numerical solution of the analytical expression for pressure in perturbation theory.

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APPENDIX D

EXPERIMENTAL PROPERTIES OF THE CH_4 + CF_4 SYSTEM

The volume of the pure liquids CH_4 and CF_4 and the volume of
the equimolar CH_4 + CF_4 mixture at P = 0, T = 111°K were estimated
from the following data given by Croll and Scott.[27]

	V at 106.7°K (cm^3/mole)	$\alpha = (1/V)(\partial V/\partial T)$ (°K)	Temp. range for α, °K
CH_4	37.17	0.00329	105÷112
CF_4	48.93	0.00259	94-107
CH_4 + CF_4 ($x_1 = x_2 = .5$)	43.85	0.0031	104-107

The resulting volumes at 111°K are as follows:

	V at 111°K (cm^3/mole)
CH_4	37.70
CF_4	49.47
CH_4 + CF_4 ($x_1 = x_2 = .5$)	44.43
Calculated excess volume of equimolar mixture	0.845

Croll and Scott give the following relation for calculating
V^E (cm^3/mole) at 106.7°K as a function of composition

$$V^E = x_1 x_2 [A + 0.86(x_1 - x_2) + 0.09(x_1 - x_2)^2] , \qquad (D-1)$$

where the constant A = 3.52, and the subscript 1 refers to CH_4.

In order to calculate V^E at 111°K as a function of composition
the calculated value of V^E (0.845 cm^3/mole) for the equimolar mixture at

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$111°K$ has been used with Eq. (D-1) to determine a different value of the constant A to be used at $111°K$. The value of A found to give the correct equimolar V^E (0.845 cm^3/mole) at $111°K$ is 3.38. This value of A is used with Eq. (D-1) to estimate $V^E_{111°K}$ at other compositions. The volume of the $CH_4 + CF_4$ mixture at $111°K$ and at compositions different from $x_1 = x_2$ is estimated by adding the calculated value of $V^E_{111°K}$ to the volume of an ideal mixture of $CH_4 + CF_4$ at $111°K$.

Excess free energy at $111°K$ is calculated as a function of composition from the following relation given by Thorp and Scott.[27]

$$G^E/RT = x_1 x_2 [1.56 + 0.36(x_1 - x_2)] , \qquad (D-2)$$

where subscript 1 again refers to CH_4.

A NEW APPROACH TO THE REFERENCE STATE FOR
LIQUID TRANSPORT PROPERTIES

Introduction

A simple approach to the reference state for liquid transport
properties explains the relation between the free volume theory of
Doolittle[42] or Cohen and Turnbull[43] and the configurational entropy
theory of J. H. Gibbs.[44,45,46] It is suggested that both theories
are based on the same reference state. In the new approach this
state is the perfectly ordered liquid with a specific volume equal
to that of the crystalline solid with a nearest neighbor separation
equal to the radius of the first peak in the experimental liquid
radial distribution function. As an approximation to this volume we
follow the lead of Eyring's significant structure theory[47] in using
the volume of the solid at the normal melting point. This reference
state satisfies the requirement of infinite viscosity, zero configurational
entropy, and zero free volume. It also reduces by one the number of
adjustable parameters in the free volume equation by fixing the
reference volume V_o as the volume of the solid at the melting point.

The theory is supported by empirical findings of Hogenboom,
Webb, and Dixon[48] for liquid hydrocarbon viscosities, by the success
of Eyring's liquid theory, and by results of correlating liquid
viscosities for argon, benzene, and molten NaCl reported herein. The
reference state predicted by the criterion of zero configurational
entropy performs well in the free volume equation for viscosity
supporting the unified view of free volume and configurational entropy.

Two Current Theories

In the past there has been considerable discussion of the glass transition in both simple liquids and polymer melts. A recent view proposed first by Gibbs and DiMarzio[44,45,46] is that the observed glass transition temperature is determined by relaxation phenomena; however, there is a lower limit to the observed glass transition that would be observed in an experiment of infinite duration provided crystallization could be prevented. The glass at this temperature and density is called by Gibbs the ground state for the amorphous liquid. Gibbs maintains that this ground state is the point at which the configurational entropy vanishes, while Cohen and Turnbull[43] identify this state as the point of disappearance of the so-called free volume (V_f) which appears in the free volume transport equations.

The theories can be formulated in terms of either temperature or molar volume. In this work the latter will be used. In its simplest form the free volume equation originally proposed by Doolittle[42] for viscosity (η) is given as follows

$$\ln \eta = A + B/V_f \qquad \text{(E-1)}$$

where

$$V_f = V - V_o \quad .$$

Here A and B are empirical constants; V is the volume per mole of the liquid, and V_o is the volume per mole of the liquid in the ground state.

Both of the above mentioned views assign to the ground state the thermodynamic significance of a fundamental reference state for

liquid transport properties. In the following development it is suggested that the two theories are based on essentially the same reference state, one which can be predicted from solid properties.

Hole Theory of the Liquid

Gibbs and DiMarzio developed their theory for prediction of the glass transition on the basis that the glass transition was a true second order transition. They felt that the glass transition intervened to prevent a paradox pointed out by Kauzmann.[49] One aspect of the paradox arose when one extrapolated liquid entropies at constant pressure to temperatures well below the freezing point. The apparent entropy of the liquid eventually became lower than that of the corresponding crystalline phase. At the same time the apparent molar volume of the liquid became less than that of the crystalline phase. Gibbs employed the canonical configurational partition function for the liquid to predict the point of the second order transition. This point was characterized by a temperature T_2 (or equivalently V_2). While Gibbs wrote the partition function for a polymer melt, this work will deal only with that for a simple liquid. The following assumptions for the simple liquid are analogous to those of Gibbs for the polymer melt:

1. The liquid can be accurately represented by a hole theory, consisting of molecules and empty spaces or of occupied and unoccupied lattice sites.

2. Vibrational contributions are not included in the definition of configurational entropy, as they are assumed to be the same in solid, liquid, and glass states.

3. The ground state for the liquid is defined as the state

    of zero configurational entropy.

For a simple liquid the configurational partition function Q^c
can be expressed as follows:

$$Q^c = \frac{(n + n_o)!}{n! \, n_o!} \, e^{-nE_o/2kT} \, v_f' \, . \tag{E-2}$$

Here n and n_o are the number of occupied and unoccupied lattice sites,
respectively. The v_f' term, not to be confused with V_f in Eq. (E-1),
arises from vibrations of molecules about their lattice sites. The
$\dot{E}_o$ represents the potential energy of a molecule located on its lattice
site, while T is the absolute temperature, and k is Boltzmann's constant.
Gibbs leaves out the vibrational factor v_f' according to assumption 2,
saying that it is unaffected by a phase transition. Thus, with
Eq. (E-2) and the usual definition of configurational entropy (S^c)

$$S^c = k \, \ln Q^c + kT^2 \left(\frac{\partial \ln Q^c}{\partial T} \right)_{n,V} , \tag{E-3}$$

we obtain neglecting the v_f' term

$$S^c = k\ln\{(n + n_o)!/(n!n_o!)\} , \tag{E-4}$$

where we assume for simplicity that n_o and E_o are functions of volume
only.

In his treatment of polymer melts Gibbs chose to neglect the
combinatorial factor $(n + n_o)!/n!n_o!$ when equating the configurational
entropy to zero on the assumption that it was near to 1.0 relative to
other terms in his expression. In the case of simple liquids, however,

it can be seen from Eq. (E-4) that when vibrational terms are neglected
the only contribution to the configurational entropy is due to the
combinatorial factor. By defining V_2 as the state at which $S^c = 0$
it is seen that this is the point at which $n_o = 0$. Thus if we define
the free volume as the volume due to the presence of vacancies in the
lattice, we have the point of zero configurational entropy coincident
with the point of zero free volume. We can also see that in this state
since $n_o = 0$ we have a perfectly crystalline phase, not an amorphous
glass as suggested by Gibbs and DiMarzio. If the dependence of n_o
on volume were known then the value of V_2 (and corresponding T_2)
could be determined as the apparent volume of the state obtained by
extrapolation to $n_o = 0$.

The Real Liquid

It is seen above that in the simple hole theory under assumptions
analogous to those of Gibbs the state of zero free volume coincides
with the state of zero configurational entropy. A case can be made
for the applicability of such a reference state in real liquids. One
must first consider the full significance of zero configurational
entropy as defined herein. First it must be said that in a real system
the vibrational contribution to configurational entropy would not be
expected to be exactly the same in the three condensed states, except
at 0°K neglecting differences in zero point energies. Only here would
the Gibbs definition of configurational entropy neglecting vibrational
terms be strictly correct. For the present purposes the configurational
entropy of a simple liquid other than that arising from vibrations
will be referred to as the structural entropy since it depends only

on the arrangement of molecules throughout the system in question. It is this structural entropy that is given in Eq. (E-4). In fact, it can be said that the only state of either the model or a real simple liquid with zero structural entropy (or configurational entropy in the Gibbs sense) would be a perfectly ordered crystalline state with no vacancies. Note that the temperature of this hypothetical state need not be 0°K. It is only required that the state is a crystalline one, since the Gibbs definition of S^c includes only the structural contribution to the entropy of a simple liquid. Thus any crystalline solid free of vacancies and structural defects would satisfy this criterion at any temperature.

The question that remains is whether there is reason to believe that such an ordered state, as opposed to the amorphous glass, is a reasonable choice for the ground state of the liquid. Experimental work of Mikolaj and Pings[50,51] on the radial distribution function for liquid argon along with the success of the Eyring significant structure theory and the recent theory of liquid structure by Bhatia[52] support such a view. The experimental results of Mikolaj and Pings show that the position of the first peak in the radial distribution function for liquid argon is very nearly constant over the range of liquid conditions studied. The position of the first peak can be interpreted as the location of the shell of nearest neighbor molecules around a given molecule. For liquid argon this peak is located at an average distance of 3.81 Å with a median of 3.84 $\pm$ .10 Å. This is near to the value of 3.885 Å corresponding to the nearest neighbor separation in solid argon at the melting point. It is also near to the value of 3.822 Å,

the location of the minimum in the Lennard-Jones potential for argon with Michels' parameter. This potential has been shown by Monte Carlo and molecular dynamics calculations to be a good effective pair potential for liquid argon. While the position of the first peak in the liquid radial distribution function is nearly constant, the coordination number (N_1) or number of nearest neighbors, calculated from the area under the first peak of the function $4\pi\rho r^2 g(r)$, increases with increasing density, where ρ is the average number density and $g(r)$ is the radial distribution function. In fact Bhatia[52] has shown that linear extrapolation of the coordination number from a value of zero at zero density yields a value of 12 in the supercooled liquid at a density near that of the solid at the melting point. At the density and temperature at which the apparent value of N_1 becomes 12 naturally N_o, the number of vacant nearest neighbor lattice sites, becomes zero. Bhatia has assumed such a linear dependence of N_1 in his theory, but the actual value of N_1 depends on which of several methods[50] are used to calculate it.

Such evidence supports the view that the solid, originally with $N_1 = 12$ in the crystalline state, expands in total volume on melting by reducing the number of nearest neighbors while keeping the nearest neighbor separation essentially constant. In the hole model discussed previously this is analogous to the introduction of vacant lattice sites in the lattice structure. From the variation of N_1 with density contraction of the liquid on cooling appears to occur by a cooperative rearrangement of the molecules to expel the excess volume that was acquired on melting. This is accomplished by more efficient packing

increasing the coordination number but still maintaining nearly the same nearest neighbor separation that existed in the solid at the melting point. This suggests that if it were possible to supercool the simple liquid to the density of the solid at the melting point without forming the glass, the liquid structure would approach smoothly the structure of the solid at the melting point at least with respect to the first coordination shell of nearest neighbor molecules. At this hypothetical point the coordination number would have increased to near 12 and the nearest neighbor separation would still be almost the same in the liquid as in the solid at the melting point. In this case the reference state or ground state of the liquid might well be taken as the perfectly ordered state with a density near that of the solid at the melting point. A more correct reference volume (V_o) would be that of the crystalline state with a nearest neighbor separation equal to the radius of the first peak in the experimental liquid radial distribution function. To the extent that this is the same as that in the solid at the melting point, the density of the solid at melting should be a good approximation to the reference state density. For argon V_o would be a slightly smaller volume than V_{sm} the volume of the solid at the melting point. With the proposed reference state the criterion of zero structural entropy would be met by virtue of the crystalline structure. Also it is the crystalline state with which we naturally associate infinite viscosity. At the same time with the free volume defined as that volume in excess of the volume of the solid at the melting point the free volume also vanishes in the reference state.

Verification of the Proposed Reference State

The recent work of Hogenboom, Webb, and Dixon[48] has shown that for five hydrocarbon liquids the V_o in Eq. (E-1) which gives the best fit of the experimental viscosity differs from the experimental volume of the solid at the melting point by an average of only 0.96%. It is interesting to note that in four of the five liquids the value of V_o was slightly smaller than V_{sm} (the volume of the solid at the melting point). This is in line with the statement made earlier in the case of argon. The above cited authors have stated that the value of V_o which gives the best fit of viscosity increases slightly with decreasing temperature and might thus equal V_{sm} in the supercooled liquid region. According to Macedo and Litovitz[53] it is the supercooled region in which Eq. (E-1) in its simple form is most applicable.

The simple view of the reference state is further supported by correlating the viscosity for three very different liquids using the free volume equation for viscosity given in Eq. (E-1). The parameter V_o which is usually found empirically as a third parameter has been taken as volume per mole of the solid at the melting point. The results of the correlations for saturated liquid argon, saturated liquid benzene, and molten sodium chloride are given in Table 38. The results are encouraging. Values of the parameters A and B which minimize the sum of squares of deviations are given in Table 39 along with the volume of the various solids at the melting point.

The simple free volume transport equations have historically performed better for the larger polyatomic molecules than for such

Table 38.   Comparison of predicted and experimental
viscosities.

Compound	T(°K)	V(cm^3/mole)	Viscosity (centipoise) predicted	experimental
Argon[a]	84.25	28.3	0.305	0.282
	86.25	28.6	0.265	0.262
	86.9	28.7	0.257	0.256
	87.3	28.8	0.248	0.252
	90.0	29.2	0.217	0.232
	99.5	30.5	0.162	0.162
	111.0	32.7	0.123	0.137
	120.0	34.5	0.108	0.116
	127.0	36.3	0.099	0.100
	133.5	39.2	0.090	0.077
Benzene[b]	288.2	88.34	7.06	6.96
	289.0	88.41	6.98	6.90
	289.5	88.50	6.88	6.92
	290.2	88.57	6.80	6.84
	293.2	88.87	6.49	6.49
	298.2	89.40	6.01	5.99
	303.2	89.95	5.59	5.66
	309.2	90.61	5.16	5.30
	313.2	91.08	4.89	4.82
	320.2	91.91	4.50	4.48
	333.2	93.43	3.94	3.95
	345.9	94.94	3.53	3.50
Sodium Chloride[c]	1090	37.783	1.37	1.38
	1100	37.905	1.32	1.32
	1110	38.029	1.27	1.27
	1120	38.178	1.21	1.22
	1130	38.303	1.17	1.17
	1140	38.454	1.13	1.12
	1150	38.581	1.09	1.08
	1160	38.734	1.05	1.04
	1170	38.863	1.01	1.01
	1180	38.993	0.98	0.98
	1190	39.149	0.95	0.95
	1200	39.281	0.92	0.92
	1210	39.413	0.89	0.89
	1220	39.573	0.86	0.87
	1230	39.735	0.84	0.84
	1240	39.870	0.81	0.82

[a]Viscosities and densities from N. F. Zhandanova, Soviet Physics,
JETP, 4, 749 (1957).

Table 38 (Continued)

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[b]Viscosities and densities from J. Timmermans, <u>Physico-Chemical Constants</u>
<u>of Pure Organic Compounds</u> (Elsevier, New York, 1950).

[c]Viscosities and densities from NSRDS-NBS-15, Molten Salts: Vol. I
Electrical Conductance, Density and Viscosity Data, National Bureau
of Standards, Oct. 1968.

Table 39. Best-fit parameters for equation (E-1).

Compound	A	B	$V_{sm} (cm^3/mole)$ [a]	rms % dev
Argon	-2.774	5.265	24.98	7.42
Benzene	0.07091	21.35	77.00	1.15
Sodium Chloride	-2.091	18.25	30.19	0.64

[a]Values for V_{sm} are those used by Eyring and co-workers: J. Walter and H. Eyring, J. Chem. Phys. 9, 393 (1941); C. M. Carlson, H. Eyring, and T. Ree, Proc. N.A.S. 46, 333 (1960).

simple molecules as argon. The poorer performance of the predicted reference volume in Eq. (E-1) for argon may be the result of the failure of the simple form of the equation rather than of the predicted reference state. The correlation for liquid argon would be improved somewhat if instead of equating V_o and V_{sm}, we take V_o equal to the volume of the solid with a nearest neighbor separation of 3.81 Å suggested by the radial distribution function data. This lowers the rms % deviation in Table 39 to 5.71.

The Glass Transition

As mentioned earlier, the mechanism of contraction proposed for the liquid requires a cooperative rearrangement. Since relaxation times in liquids increase with decreasing temperature, it is reasonable to expect that for a given liquid there exists a temperature T_1 below which such a cooperative rearrangement is extremely unlikely during the duration of an experiment. Below this temperature the liquid would be expected to contract by simply shrinking the existing structure of the liquid as no cooperative phenomena would be involved. In this region the nearest neighbor number N_1 would cease to be a variable, and the previously constant nearest neighbor distance would vary as the cube root of the volume as is the case in crystalline solids. This change from one mode of contraction to the other would be expected to occur not at one particular temperature but over a temperature range. The amorphous character of the liquid that existed at the lower limit of this temperature range T_1 would be expected to be frozen in at all temperatures below T_1. Such is the case with the glass transition.

Kauzmann[49] has pointed out that, while there are no discontinuous changes in volume and heat content as the liquid goes through the glass transition, once the glass has formed changes in volume and energy with temperature are similar in magnitude to those of a crystalline solid.

Using the free volume equation, Carpenter, Davies and Matheson[54] have had some success in predicting the glass transition point as the point at which $\eta = 10^{13}$ poise. Such success indicates that attempts to identify the reference state, which in the free volume equations is by definition one of infinite viscosity, with the glass transition are incorrect. Rather, it is suggested that the simple view of the reference state proposed in the present work is more reasonable. It should also be noted that with the present definition of the reference state the Kauzmann paradox is eliminated, since the reference state represents the end to any reasonable extrapolation of liquid properties to high densities.

Conclusions

A simple view of the reference state for liquid transport properties satisfies the Gibbs requirement of zero configurational entropy and the Doolittle or the Cohen and Turnbull requirement of zero free volume. The reference state is taken to be the perfectly crystalline phase with a nearest neighbor separation equal to that in the liquid. The volume of this phase is taken to be approximately equal to the volume of the solid at the melting point. It has been shown that the proposed approximation to the reference state volume (V_o) can be used to correlate liquid viscosities in the simplest form of the free volume

viscosity equation. It should be mentioned at this point that attempts to define V_o as the close-packed molecular volume[53] contain the assumption that infinite viscosity is associated only with a state in which molecular motion is impossible as molecules are faced with essentially infinite potential energy barriers in all directions. The new approach outlined in this work capitalizes on the fact that this is certainly not a necessary condition, as would be seen in the case of infinite viscosity in the crystalline solids with a volume greater than the close-packed volume. It is suggested that it is the vanishing of the structural contribution to configurational entropy resulting in a perfect crystalline state that is correctly associated with infinite liquid viscosity. The use of the density of the solid at the melting point as the reference density for the liquid is in accordance with the emphasis which Eyring's significant structure theory has placed on this experimental quantity. Eyring's expression for liquid viscosity likewise yields infinite viscosity when the liquid volume equals the volume of the solid at the melting point.

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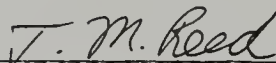21. T. W. Leland, J. S. Rowlinson and G. A. Sather, Trans. Faraday Soc. 64, 1447 (1968).

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BIOGRAPHICAL SKETCH

Donald William Calvin was born April 26, 1945, at Princeton, Indiana. At the age of six, he moved with his family to Oak Ridge, Tennessee, where he enjoyed five years in the foothills of the Great Smokey Mountains. His family then moved to Baton Rouge, Louisiana, where the bayou country provided a pleasant setting for the remainder of his education through the baccalaureate level. In May of 1967, he was married to the former Barbara Gene Beaucoudray of Baton Rouge. Upon receipt of a Bachelor of Science Degree in Chemical Engineering at Louisiana State University in January of 1968, he moved to Gainesville, Florida, to pursue graduate education toward the degree of Doctor of Philosophy in the Department of Chemical Engineering at the University of Florida. Here the pleasant Florida living made the demands of graduate study seem less severe and provided an excellent atmosphere for the early childhood of his daughter, Sandy, born October, 1968.

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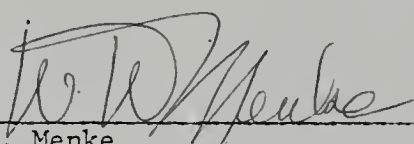
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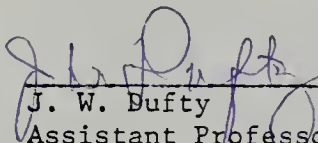
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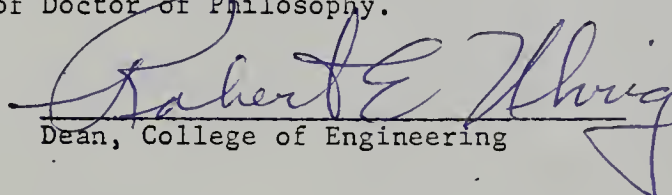Associate Professor of Chemical Engineering

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